Génie chimique

Chemical Engineering

UNIVERSITÉ D'OTTAWA
UNIVERSITY OF OTTAWA

3-9003

CONTRACT SERIAL NUMBER: OSU82-00416

REQUISITION NUMBER: 23440-3-9003

CONTRACTOR: University of Ottawa

Filtration and Precipitation Characteristics of Yellow Cake: Determination of the Critical factors in the Precipitation of Uranium from Sulfonate Solutions Using Experimental Design Techniques

J.A. Golding & J. Hopkins
Chemical Engineering Department
University of Ottawa
Ottawa, Ontario
K1N 9B4

AUG 19 1988

MICROMEDIA

92 pp

ABSTRACT

The effects of operating variables upon the precipitation properties of uranium from aqueous solution using hydrogen peroxide have been evaluated. The reactions was:

$$UO_2(SO_4)_3^{4-} + 2H_2O + H_2O_2 \rightarrow UO_4.2H_2O + 3SO_4^{2-} + 2H^+$$

The operating variables studied were; 1) the initial uranium concentration, 2) the amount of hydrogen peroxide added, 3) the precipitation pH, 4) sulphate concentration in the solution, 5) the residence time in the precipitator. The effects of these operating variables upon the following precipitation properties were evaluated; 1) filtercake yield, 2) amount of uranium precipitated, 3) concentration of uranium in barrens, 4) the conversion, 5) uranium content of the cake, 6) sulphur content of the cake, 7) particle size, 8) particle size distribution.

The effects of the operating variables upon the responses were determined by obtaining the parameters of an empirical model of the form

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \ldots + \beta_{12} x_1 x_2 + \ldots + \beta_{45} x_5 x_5 + \ldots + \beta_{55} x_5^2$$

A two level fractional factorial design was used as the basis for two experimental plans to screen out any insignificant effects. These two experimental plans were; 1) a central composite design and 2) the fractional factorial design with added centrepoints. The adequacy of the resultant models was evaluated using a quantitative lack of fit test. In general, the models describing the system responses derived from the central composite design did not pass this test. For the fractional factorial with centerpoints, most of the response variables were adequately modelled.

The resultant models indicated that the responses were primarily dependent upon the initial uranium content of the solution however the filtercake yield and

uranium content of the barrens were found to depend on the precipitation pH. The amount of uranium precipitated was found to be affected by the initial uranium concentration, the amount of hydrogen peroxide added and the total sulphate in the solution. The concentration of uranium in the barrens was not adequately modelled by either experimental design, however, the resultant parameter values were consistent with what would be expected from a mass balance on the uranium. The amount of uranium precipitated and the uranium concentration of the barrens varied in opposite directions as the operating variables were changed.

Overall, the results indicated that the responses could be adequately represented by simple linear equations. The experimental design techniques could be used for control of an actual uranium mill that may be considering a changeover to the hydrogen peroxide precipitation method.

TABLE OF CONTENTS

Section	Page
ABSTRACT	i
TABLE OF CONTENTS	iii
LIST OF TABLES	v
LIST OF FIGURES	vii
1. INTRODUCTION	1
1.1 Research in Uranium Precipitation	3
1.2 Crystal Growth	6
2. LEAST SQUARES EQUATIONS AND EXPERIMENTAL DESIGN	9
2.1 Experimental Design	12
2.2 Statistical Test	20
3. EXPERIMENTAL PROCEDURE	22
3.1 Introduction	22
3.2 pH Measurement	23
3.3 The Determination of the Uranium Values	23
3.4 Particle Size Analysis	23
4. RESULTS AND DISCUSSION	24
4.1 Analysis of Results	24
4.2 Filtercake Yield	24
4.3 Uranium Precipitated	31
4.4 Barrens Concentration	43
4.5 Conversion	48
4.6 Uranium Content	51
4.7 Sulphur Content	51

4.8 Size and Size Distribution 58

FILTRATION RATES 59

5. CONCLUSIONS AND RECOMMENDATIONS 63

6. REFERENCES 65

NOMENCLATURE 67

APPENDIX A - EXPERIMENTAL RESULTS 70

LIST OF TABLES

Table		Page
2.1	Design Region of Operating Variables	13
2.2	The Operating Values of the Experimental Runs	14
2.3	Coded Values of the Operating Variables	16
2.4	The Alternative Values for Cases 2,3, and 4	18
2.5	Means and Variances of the Response Variables at the Design Centrepoint	22
4.1	Range of Operating Variables Studied	25
4.2	Plausible Models for the Filtercake Yield for Experimental Plan I	26
4.3	Plausible Models for the Filtercake Yield for Experimental Plan II	33
4.4	Plausible Models for the Uranium Precipitated for Experimental Plan I	36
4.5	Plausible Models for the Uranium Precipitated for Experimental Plan II	39
4.6	Plausible Models for the Barrens Concentration for Experimental Plan I	45
4.7	Plausible Models for the Barrens Concentration for Experimental Plan II	46
4.8	Plausible Models for the Conversion for Experimental Plan I	49
4.9	Plausible Models for the Conversion for Experimental Plan II	50

4.10	Plausible Models for the Uranium Content of the Filtercake for Experimental Plan I	52
4.11	Plausible Models for the Uranium Content of the Filtercake for Experimental Plan II	53
4.12	Plausible Models for the Sulphur Content of the Cake for Experimental Plan I	55
4.13	Plausible Models for the Sulphur Content of the Cake for Experimental Plan II	57
4.14	Plausible Models for the Mean Particle Size for Experimental Plan I	60
4.15	Plausible Models for the Mean Particle Size for Experimental Plan II	61
4.16	Plausible Models for the Size Distribution for Experimental Plan II	62
A-1	EXPERIMENTAL RESULTS	70
A-2	EXPERIMENTAL RESULTS	72
A-3	PARTICLE SIZE DISTRIBUTIONS	74

LIST OF FIGURES

Figure		Page
4.1	Resultant Model for Filtercake Yield for Plan I - Model 1/1	28
4.2	Resultant Model for Filtercake Yield for Plan I - Model 2/2	29
4.3	Resultant Model for Filtercake Yield for Plan I - Model 3/1	30
4.4	Effect of Initial Uranium Concentration upon the Filtercake Yield Excluding Run Number 19	32
4.5	Effect of Initial Uranium Concentration upon the Filtercake Yield for Plan II	34
4.6	Resultant Model for Filtercake Yield for Plan II - Model 1/2	35
4.7	Resultant Model for the Amount of Uranium Precipitated for Plan I - Model 1/1	38
4.8	Resultant Model for the Amount of Uranium Precipitated for Plan I - Model 2/1	40
4.9	Resultant Model for the Amount of Uranium Precipitated for Plan I - Model 3/1	41
4.10	Resultant Model for the Amount of Uranium Precipitated for Plan I - Model 4/1	42
4.11	Resultant Model for the Amount of Uranium Precipitated for Plan II - Model 1/1	44

4.12 The Effect of pH upon the Barrens Concentration at the Centrepoint 47

4.13 The Effect of pH upon the Uranium Content of the Cake 54

1. INTRODUCTION

The precipitation of uranium from aqueous solutions to form yellowcake is an important step towards the final fuel used in nuclear reactors. It is necessary for the yellowcake to be of high purity, have good filtration characteristics, and to dry readily. Yellowcake should also have good material handling characteristics. A number of methods for obtaining yellowcake from a uranium solution are in use. Of the precipitation methods available, the precipitation of the uranium with ammonia to form ammonium diuranate is the one most frequently used in North America. Ammonium diuranate is generally of high quality, however, specifications that must be met regarding impurity levels are becoming more stringent. Also, the ores presently being processed are of a lower grade than those processed in the past. As a result hydrogen peroxide precipitation may be considered as an alternative in the future, since this precipitation method yields a high purity product under a wide range of conditions. In order to convert from one precipitation method to another, it is necessary to know how the properties of the uranium solution affect the characteristics of the precipitation. Some of the critical factors include:

1) the initial uranium concentration
2) the H_2O_2/U molar ratio
3) the excess sulphate in the solution
4) the precipitation pH
5) the residence time in the precipitator.

Other variables that could be considered are the mixing characteristics, temperature and impurity levels in the solution. These variables were not

studied in this work, but could be part of the experimental design in an actual plant.

Most of the research in hydrogen peroxide precipitation of uranium as been directed towards determining how the above factors affect the barrens concentration (i.e. uranium concentration in the filtrate). One of the objectives of this study was to extend this work to determine how other characteristics of the precipitation were affected by the operating variables. These characteristics include filtercake yield, uranium content of the cake, the amount of uranium precipitated, the sulphur content of the cake, and the particle size and size distribution of the precipitate. Filtercake yield differs from the amount of uranium precipitated by the fact that the filtercake will contain impurities such as hydrated water and some residual moisture which would have to be removed later in drying operations. The amount of uranium precipitated is a measure of the efficiency of the reaction.

In addition, knowledge of the major parameter affecting precipitation characteristics would be of great assistance in future work involved with studies on the actual mechanism of the precipitation reaction.

If hydrogen peroxide precipitation is to be considered by a uranium mill without any major changes being made to rest of the process, it would be of particular importance to evaluate the effects of process variables upon the precipitation properties. A method which will measure the effects of process variables upon a group of response variables is experimental design. In this study, two different experimental designs were used. Both experimental designs used a 2^5 factorial design as a basis: one design being a central composite design, the other being a fractional factorial design with the centrepoints included. This method of experimentation involves fitting experimental data to an empirical linear model which allows for the screening out of unimportant variables. The

disadvantages of the experimental design methods employed in this study are the inabilities to extrapolate beyond the experimental points and to derive the parameters in a complex mechanistic model. These experimental designs are also limited to data which can be well described by a simple polynomial (i.e. the data is not highly non linear in nature). The effectiveness of the resultant linear equations in describing system behaviour has been evaluated to determine whether the possibility exists of employing these methods for describing the system in an actual uranium mill.

1.1 Research in Uranium Precipitation

Research in uranium precipitation is limited by the fact that the results depend heavily upon the characteristics of the system under study. Some of the results of research in uranium precipitation are as follows.

The precipitation of uranium by ammonia from aqueous solutions has been studied with varying results (13-17). Tomazic et al. (13) studied the system $UO_2(NO_3)_2$ - NH_4OH-NH_4-NO_3. It was found that precipitation will occur only at certain levels of pH, and of ammonia concentrations. Precipitation depended upon the initial ratio of $NH_4OH/UO_2(NO_3)_2$. It was observed that there was a sudden pH drop upon the initiation of the reaction.

For the same system, Stuart and Whately (14) used infra-red spectrophotometry and thermal analysis to discover that the formula for ammonium diuranate is in fact an "average" chemical formula. Rather that being $(NH_4)_2U_2O_7$, ammonium diuranate has a changing ratio of NH_3:u within its structure. The actual reaction between $UO_2(OH)_2$ and NH_3 is as follows:

$$UO_2(OH)_2 + xNH_4^+ \rightarrow UO_2(OH)_{2-x} \cdot (O\text{-}NH_4^+)_x + xH^+ \qquad (1.1.1)$$

Merino (15), studied the precipitation of ammonium diuranate with the purpose of determining how operating conditions in the precipitator affected the thickening, filtering, stirring, pumping and drying properties of the yellowcake.

The temperature of the precipitator was varied, continuous and batch precipitators were used, and both NH_4OH and gaseous NH_3 were used. It was observed that adjusting the operating variables to make the properties of the suspension more suitable for further processing such as settling and filtration could adversely affect the U_3O_8 content of the final product.

Rodriguez (16) investigated the recovery of uranium from the Purlex process using ammonia. It was observed that sulphate levels in the cake can be kept within the refiner's specification limits by manipulating the precipitation temperature and keeping it between 30-40°C. It was recommended that the product be calcined at 700°C.

Bryson (17) studied the electrolytic precipitation of ammonium diuranate from sulphate solutions. The reaction took place in the cathode department of an electrolytic cell. He discovered that the precipitation and settling rates of the ammonium diuranate were correlated with the current consumption. The two factors, however, were found to be inversely correlated. In other words, to increase the settling rate, the current had to be decreased, but a decrease in yield resulted.

In the case of hydrogen peroxide precipitation, the research has been concerned with reducing the concentration of uranium in the barrens solution (12, 18-22). In some studies, however, the kinetics of the reaction have been considered (19,20). Brown (12) studied the effect of a number of operating conditions upon the barrens of the process. He recognized the fact that operating conditions in individual mills vary and developed a theoretical model to predict the barrens concentration for given concentrations of sulphate and chloride, pH, and precipitation time. The model was based upon the chemical equilibria created between UO_2^{2+} with SO_4^{2-} and Cl^-. The model that was given to describe the barrens concentration on a U_3O_8 basis was:

$$U_3O_8(g/l) = (10^{-pH})^2 \times (1+710[SO_4]^2/96+0.88[Cl]/35.5)/\ 3x[H_2O_2]xK_{H_2O_2}/810x34 \quad (1.1.2)$$

Brown also expressed $K_{H_2O_2}$ and $[H_2O_2]$ as functions of time (12).

$$K_{H_2O_2} = K_o + t^2/(1 + 0.0075t^2) \quad (1.1.3)$$

$$[H_2O_2] = [H_2O_2]_0\ [1 - K_{dec}{}^{3}\sqrt{t}-.67\ ]\ ([U_3O_8]_0 - [U_3O_8]_t)/[U_3O_8]_0 \quad (1.1.4)$$

where K_{dec} was a decomposition constant for H_2O_2.

By performing a number of batch precipitations, the theoretical model was compared with an empirical model based upon the interactions of the variables upon the barrens concentration. It was noted that the theoretical model tended to underestimate the barrens concentration and that the empirical model agreed more closely with the experimental data. The empirical model was not given.

Shabbir and Tame (18) performed batch tests on the same system to measure the effect of a different set of variables upon the barrens and purity. A synthetic stock solution was prepared with molybdenum and vanadium included to determine how purity was influenced by their presence. The effect of temperature upon the barrens concentration and Mo and V levels in the precipitate was measured. The effect of pH upon the same two variables was measured. It was concluded that the reaction required more than the stoichiometric amount of peroxide, the precipitation was dependent upon pH, while the vanadium content of the cake was lowered if the reaction pH was increased to 5. Increased temperature resulted in an increase in the reaction rate, but an increase in the vanadium and molybdenum concentrations in the cake was also observed. It was also observed that increased sulphate levels slowed down the rate of reaction.

Using a spectrophotometer to measure the change of U(IV) concentration with time, Bhattacharyya, et al. (19,20) studied the kinetics of the reaction

$$U(IV) + H_2O_2 \rightarrow U(VI) + 2H^+ \qquad (1.1.5)$$

in the presence of both sulphate and chloride.
Their results indicated that the reaction could be described by the biomolecular rate equation

$$\frac{-d}{dt}[U(IV)] = k_{obs}[U(IV)][H_2O_2] \qquad (1.1.6)$$

$k_{obs} = f([H^+]^{-1.3})$ for hydrochloric acid medium
$k_{obs} = f([H^+]^{-.55})$ for sulphuric acid medium.

It was also found that k_{obs} was a function of equilibrium constants of uranium/sulphate or uranium/chloride complexes suspected of participating in the reaction mechanism.

The implication of these studies was that the rate of particle growth of the uranium precipitate would depend upon the concentration of sulphate, uranium, and peroxide and the pH since this growth would be dependent upon the concentration of U(VI).

1.2 Crystal Growth

The particle size and size distribution is of importance when considering ways to increase the filtration and drying rates of a filtercake. Since both of these properties are dependent upon the specific surface area of the filtercake, it is possible that a change in operating conditions could be found that will produce favourable characteristics. Such a change would be beneficial to the

mill operator. However, the operator must assess whether these changes adversely affect the quality and yield of the cake. Precipitation differs from crystallization by the means to which supersaturation takes place. In a crystallization operation, supersaturation is achieved by cooling the solution or removal of solvent by evaporation. In precipitation operations, the supersaturation is achieved by transforming the desired product from a soluble species to a virtually insoluble species by means of a chemical reaction. In the present study, for example, the soluble uranium species is uranyl sulphate as $UO_2(SO_4)_3^{4-}$ and the insoluble species is $UO_4.2H_2O$.

Crystal growth is a mass transfer operation and as such is dependent upon the surface area and the concentration gradient. The mechanism involves; 1) a migration of molecules from the bulk solution to the interface between the solution and particle with diffusion through this interface, 2) a surface "reaction" or absorption of the particle upon the crystal surface. In terms of the rate of mass deposited over time these two mechanisms may be written as;

$$\frac{dm}{dt} = k_d A(C-C_i) \qquad (1.2.1)$$

$$\frac{dm}{dt} = k_r A(C_i-C^*) \qquad (1.2.2)$$

where k_d is the diffusion mass transfer coefficient

A is the surface area of the crystals

k_r is the surface "reaction" mass transfer coefficient

C is the bulk concentration of the crystalizing species in the solution

C_i is the interfacial concentration

C* is the solubility of the crystallizing species.

All terms are in consistent units.

By combining the above equations;

$$\frac{dm}{dt} = K_G A(C-C^*) \tag{1.2.3}$$

where $$\frac{1}{K_G} = \frac{1}{k_d} + \frac{1}{k_r} \tag{1.2.4}$$

The above equation may be written in terms of the particle radius by dividing both sides of the above equation by the particle density and the surface area when assuming a spherical crystal it becomes:

$$\frac{dr}{dt} = \frac{K_G}{\rho}(C-C^*) \tag{1.2.5}$$

Therefore, the crystal growth rate may be determined using the particle size distribution and measuring the rate change of the mean particle size with time. The remainder of the particle size distribution may be used to calculate the nucleation rate by applying the population balance method developed by Randolph and Larson (23).

Precipitation offers some unique factors in this kind of analysis. First of all, the concentration of the insoluble species in the bulk solution will depend upon the reaction rate between the soluble species and the precipitating agent. This means that the bulk concentration may change with time due both to the fact that it is being generated by the precipitating reaction and is also removed by the crystallization process. Hence, the rate of crystallization would depend upon the rate of formation of the insoluble species. Secondly, given that the crystallizing species is insoluble, the supersaturation ratio, $S(=C/C^*)$ is virtually infinity. This could result in the spontaneous formation of a large number of extremely small uniformly sized particles which may mean that the

crystal growth rate cannot be determined. Another phenomenon associated with precipitate is agglomeration. Agglomeration is a result of the formation of small particles. The forces needed to bind these particles together is also small leading to the formation of an agglomerate. This agglomeration has been observed to be time dependent. It may be possible to control this rate of agglomeration by control ling the precipitator conditions. Again, the effect of changing these conditions upon the other characteristics of the cake should be considered.

2. LEAST SQUARES EQUATIONS AND EXPERIMENTAL DESIGN

When using linear least squares, the objective is to fit data to an equation such as:

$$Y = \beta_0+\beta_1x_1+\beta_2x_2+\beta_{12}x_1x_2+\beta_{11}x_1^2+\beta_{22}x_2^2++ \tag{2.1}$$

This is accomplished by minimizing the sum of squares of the residuals, i.e.

$$\sum_{u=1}^{n} e_u^2 = \sum_{u=1}^{n} (Y_u -(\beta_0+\beta_1x_1+\beta_2x_2+\beta_{12}x_1x_2+\beta_{11}x_1^2+\beta_{22}x_2^2))^2 \tag{2.2}$$

This expression is minimized when the partial derivatives with respect to the parameters are set equal to zero, e.g.

$$\frac{\partial}{\partial\beta_0}\left(\sum_{u=1}^{n} e_u^2\right) = 0$$

$$\frac{\partial}{\partial\beta_1}\left(\sum_{u=1}^{n} e_u^2\right) = 0$$

.

.

.

$$\frac{\partial}{\partial \beta_{22}} \left(\sum_{u=1}^{n} e_u^2 \right) = 0$$

In matrix form, the equations may be written as:

$$\underline{X}^T \underline{X} \, \underline{\beta} = \underline{X}^T \underline{Y} \tag{2.3}$$

To solve for $\underline{\beta}$:

$$\underline{\beta} = (\underline{X}^T \underline{X})^{-1} (\underline{X}^T \underline{Y}) \tag{2.4}$$

$\underline{X}^T \underline{X}$ is a p x p matrix and $\underline{X}^T \underline{Y}$ is a p x 1 vector where p is the number of parameters in the equation.

If there are non-zero values for the off-diagonal terms in the matrix, $\underline{X}^T \underline{X}$, then, correlation among the parameter estimates will occur. This correlation may be reduced if the independent variables are redefined as

$$x_i = \frac{X_i - \bar{X}_i}{\frac{1}{2} \text{ Range of } X} \tag{2.5}$$

where x_i = coded form of X_i

X_i = actual value of X_i

For the case of a model without quadratic effects, it is possible to design a series of experiments that does not have any parameter correlation. If a series of experimental runs is predetermined at a specific set of points, then all parameter correlation can be eliminated because the experimental runs in coded form will result in all off-diagonal terms of the $\underline{X}^T \underline{X}$ matrix being zero. Hence, the parameter value, β_i, will depend only upon the value of $\sum_{u=1}^{n} (x_{iu} y_u)$ for any given run.

The procedure for determining where experiments should be performed is as follows:

1) determine the range of the operating variables
2) set up a grid of the $\underline{X}$ matrix in coded form in the following manner.
   a) all values of $x_0 = 1$
   b) the values of $x_1 = -1$ for odd numbered runs
      $= 1$ for even numbered runs
   c) the values of $x_2 = -1$ for u = 1,2,5,6,...
      $= 1$ for u = 3,4,7,8,...
   d) the values of $x_i = -1$ for 2^{i-1} runs
      $= 1$ for 2^{i-1} runs

The significance of the parameters may be evaluated for screening purposes by determining the 95% confidence intervals of the parameters using a t-distribution.

$$\beta_i = \hat{\beta}_i \pm t_v \sqrt{\text{Var}\ (\beta_i)} \tag{2.6}$$

where Var $(\beta_i) = c_{ii}$ where c_{ii} is the term in the matrix

$$\underline{C} = (X^T \underline{X})\sigma^2 \tag{2.7}$$

σ^2 = estimated pure error variance = SSR/(n-p)

v = the degrees of freedom associated with σ^2

= n-p

If 0 falls within the confidence interval, then the parameter may be dropped. If the parameter estimates are uncorrelated, then dropping of any insignificant terms will not change the values of the significant parameters.

2.1. Experimental Design

An experimental design approach was used in this study to determine the location of experimental runs. The particular design used was a half fraction of a 2^5 design with time confounded with the other four variables. The variables under question are given in Table 2.1. Centrepoints and axial points were also run to yield a central composite design. The experimental design points for the 36 runs of the study are given in Table 2.2. Experimental points 1 through 16 comprise the 2^5 fractional factorial design component, runs 17 through 26 are the axial points and runs 27 through 36 are the centrepoints. As may be seen from Table 2.2, the experimental pH values were not the same as the design values. This caused a certain amount of correlation in the parameter estimates. Hence, the significance of the initial values of the parameter estimates was evaluated for 80, 90 and 95% confidence intervals to ensure that important terms were not dropped. Three models were therefore obtained for each case.

In analyzing the data, two different experimental plans were considered. Experimental Plan I consisted of using all of the experimental points to determine the significance of any quadratic effects. In experimental Plan II the axial runs were not used and only main and second order interaction effects were determined. In practice, experimental Plan II would be the more economical plan.

Along with determining the significance of the parameter estimates at three levels of confidence, the effect of representation of the variables was considered. Instead of using pH, this variable was represented as $[H^+]$, the amount of H_2O_2 added in grams rather than the H_2O_2/U ratio was used, and the total sulphate rather than the excess sulphate was used. These new representations have been indicated by using an asterisk.

In all, 4 cases were studied. Referring to Tables 2.3 and 2.4, which give

Table 2.1

Design Region of Operating Variables

Initial Uranium Content, X_1 (g/l)	Initial Fraction of Stoichiometric Ratio, X_2 (g mol U/g mol H_2O_2)	Precipitation pH, X_3	Excess Sulphate, X_4 (g/l)	Time, X_5 (hr)
10.0	.75	2.40	0	1
12.5	1.50	2.85	4.4	2
15.0	2.25	3.30	8.8	3
17.5	3.00	3.75	13.2	4
20.0	3.75	4.20	17.6	5

Table 2.2

The Operating Values of the Experimental Runs

Run Number	X_1	X_2	X_3	$(pH_{expt.})$	X_4	X_5
1	12.5	1.50	2.85	(2.83)	4.4	4
2	17.5	1.50	2.85	(1.81)	4.4	2
3	12.5	3.00	2.85	(2.11)	4.4	2
4	17.5	3.00	2.85	(3.07)	4.4	4
5	12.5	1.50	3.75	(7.20)	4.4	2
6	17.5	1.50	3.75	(7.85)	4.4	4
7	12.5	3.00	3.75	(7.84)	4.4	4
8	17.5	3.00	3.75	(5.00)	4.4	2
9	12.5	1.50	2.85	(3.26)	13.2	2
10	17.5	1.50	2.85	(1.79)	13.2	4
11	12.5	3.00	2.85	(2.60)	13.2	4
12	17.5	3.00	2.85	(2.92)	13.2	2
13	12.5	1.50	3.75	(6.80)	13.2	4
14	17.5	1.50	3.75	(8.34)	13.2	2
15	12.5	3.00	3.75	(3.32)	13.2	2
16	17.5	3.00	3.75	(4.65)	13.2	4
17	10.0	2.25	3.30	(8.90)	8.8	3
18	20.0	2.25	3.30	(3.22)	8.8	3
19	15.0	.75	3.30	(3.72)	8.8	3
20	15.0	3.75	3.30	(3.63)	8.8	3
21	15.0	2.25	2.40	(1.55)	8.8	3
22	15.0	2.25	4.20	(4.29)	8.8	3

Table 2.2 (Cont'd)

Run Number	X_1	X_2	X_3	$(pH_{expt.})$	X_4	X_5
23	15.0	2.25	3.30	(3.09)	0	3
24	15.0	2.25	3.30	(7.67)	17.6	3
25	15.0	2.25	3.30	(3.65)	8.8	1
26	15.0	2.25	3.30	(3.50)	8.8	5
27	15.0	2.25	3.30	(2.94)	8.8	3
28	15.0	2.25	3.30	(4.74)	8.8	3
29	15.0	2.25	3.30	(4.22)	8.8	3
30	15.0	2.25	3.30	(4.28)	8.8	3
31	15.0	2.25	3.30	(6.60)	8.8	3
32	15.0	2.25	3.30	(5.40)	8.8	3
33	15.0	2.25	3.30	(3.29)	8.8	3
34	15.0	2.25	3.30	(3.80)	8.8	3
35	15.0	2.25	3.30	(3.09)	8.8	3
36	15.0	2.25	3.30	(4.25)	8.8	3

Table 2.3

Coded Values of the Operating Variables

Run Number	X_1	X_2	X_3	X_4	X_5
1	-1	-1	- .4182	-1	1
2	1	-1	- .6958	-1	-1
3	-1	1	- .6141	-1	-1
4	1	1	- .3529	-1	1
5	-1	-1	.7709	-1	-1
6	1	-1	.9478	-1	1
7	-1	1	.9450	-1	1
8	1	1	.1722	-1	-1
9	-1	-1	- .3012	1	-1
10	1	-1	- .7012	1	1
11	-1	1	- .4808	1	1
12	1	1	- .3937	1	-1
13	-1	-1	.6620	1	1
14	1	-1	1.0811	1	-1
15	-1	1	- .2849	1	-1
16	1	1	.0770	1	1
17	-2	0	1.2335	0	0
18	2	-2	-.3125	0	0
19	0	2	-.1765	0	0
20	0	0	-.2010	0	0
21	0	0	-.7670	0	0
22	0	0	-.0214	0	0
23	0	0	-.3479	-2	0

Table 2.3 (Cont'd)

Run Number	X_1	X_2	X_3	X_4	X_5
24	0	0	.8983	2	0
25	0	0	- .1955	0	-2
26	0	0	- .2364	0	2
27	0	0	- .3887	0	0
28	0	0	.1011	0	0
29	0	0	- .0404	0	0
30	0	0	- .0241	0	0
31	0	0	.6072	0	0
32	0	0	.2807	0	0
33	0	0	- .2935	0	0
34	0	0	- .1547	0	0
35	0	0	- .3479	0	0
36	0	0	- .0323	0	0

Table 2.4

The Alternative Values for Cases 2, 3, and 4

Run Number	H_2O_2 Concentration (g/l)	Coded X_2^*	H^+ Concentration (mol/l)	Coded X_3^*	Total SO_4^{2-} (g/l)	Coded X_4^*
1	2.68	-.3333	1.4791×10^{-3}	- .0527447	19.84	- .8511
2	3.75	-.1667	1.5488×10^{-2}	.9413789	26.02	- .1489
3	5.36	.0833	7.7625×10^{-3}	.3131398	19.84	- .8511
4	7.50	.4167	8.5114×10^{-4}	- .0973073	26.02	- .1489
5	2.68	-.3333	6.3096×10^{-8}	- .1577010	19.84	- .8511
6	3.75	-.1667	1.4125×10^{-8}	- .1577054	26.02	- .1489
7	5.36	.0833	1.4454×10^{-8}	- .1577054	19.84	- .8511
8	7.50	.4167	1.0000×10^{-5}	- .1575282	26.02	- .1489
9	2.68	-.3333	5.4954×10^{-4}	- .1187095	28.64	.1489
10	3.75	-.1667	1.6218×10^{-2}	.9931746	34.82	.8511
11	5.36	.0833	2.5119×10^{-3}	.0205422	28.64	.1489
12	7.50	.4167	1.2023×10^{-3}	- .0723907	34.82	.8511
13	2.68	-.3333	1.5849×10^{-7}	- .1576952	28.64	.1489
14	3.75	-.1667	4.5709×10^{-9}	- .1577061	34.82	.8511
15	5.36	.0833	4.7863×10^{-4}	- .1237415	28.64	.1489
16	7.50	.4167	2.2387×10^{-5}	- .1561178	34.82	.8511
17	3.21	-.2500	1.2589×10^{-9}	- .1577063	21.15	- .7023
18	6.43	.2500	6.0258×10^{-4}	- .1149471	33.51	.7023
19	1.61	-.5000	1.9055×10^{-4}	- .1438360	27.33	0
20	8.04	.5000	2.3442×10^{-4}	- .1410711	27.33	0
21	4.82	0	2.8184×10^{-2}	1.8422936	27.33	0
22	4.82	0	5.1286×10^{-5}	- .1540670	27.33	0
23	4.82	0	8.1283×10^{-4}	- .1000257	18.53	-1

Table 2.4 (Cont'd)

Run Number	H_2O_2 Concentration (g/l)	Coded X_2^*	H^+ Concentration (mol/l)	Coded X_3^*	Total SO_4^{2-} (g/l)	Coded X_4^*
24	4.82	0	2.1380×10^{-8}	- .1577049	36.13	1
25	4.82	0	2.2387×10^{-4}	- .1418198	27.33	0
26	4.82	0	3.1623×10^{-4}	- .1352660	27.33	0
27	4.82	0	1.1482×10^{-3}	- .0762305	27.33	0
28	4.82	0	1.8197×10^{-5}	- .1564151	27.33	0
29	4.82	0	6.0256×10^{-5}	- .1534305	27.33	0
30	4.82	0	5.2481×10^{-5}	- .1539822	27.33	0
31	4.82	0	2.5119×10^{-7}	- .1576886	27.33	0
32	4.82	0	3.9811×10^{-6}	- .1574239	27.33	0
33	4.82	0	5.1286×10^{-4}	- .1213124	27.33	0
34	4.82	0	1.5849×10^{-4}	- .1464596	27.33	0
35	4.82	0	8.1283×10^{-4}	- .1000257	27.33	0
36	4.82	0	5.6234×10^{-5}	- .1537159	27.33	0

the operating variables in terms of their coded from, the four cases were:

Case 1 The data were analyzed with the original variables X_1, X_2, X_3, X_4 and X_5.

Case 2 The data were analyzed using $[H^+]$ rather than pH., i.e. the effects of X_1, X_2, X_3*, X_4 and X_5.

Case 3 The variables X_2 and X_4 were replaced in Case 1 with X_2* and X_4* to analyze the effect of X_1, X_2*, X_3, X_4* and X_5.

Case 4 The three variables X_2, X_3 and X_4 were all replaced to analyze the responses based upon X_1, X_2*, X_3*, X_4* and X_5.

2.2 Statistical Tests

Two statistical tests were also performed to analyze the resultant models. These were the Q-test and the R-test.

The Q-test

A Q-test is used to determine the necessity (or significance) of the individual terms in a model. Because of the correlation between parameters encountered in this study due to pH control difficulties, it was felt that some significant terms may not appear. Therefore, in cases encountered in this study where different terms appeared for the 80, 90 and 95% confidence intervals, the Q-test was applied. This test is as follows:

$$Q = \frac{1}{\sigma^2} \frac{(\text{SSR from Model A}) - (\text{SSR from Model B})}{(\text{Number of parameters in Model B}) \quad (\text{Number of Parameters in Model A})} \tag{2.8}$$

where SSR = sum of squares of the residuals

n = # of experimental runs

σ^2 = SSR/(n-p) for model with the most terms (i.e. Model B)

p = # of parameters in this model

The ratio, Q, was compared with $F_{0.05\ v_1\ v_2}$ where v_1 was the difference in the number of parameters of models A and B and v_2 was the value of n-p for model

B. If Q was larger than F, then the need for the extra terms was considered significant (i.e. the extra terms were needed). This was a significance test of the null hypothesis that all of the true values of the additional parameters of model B were zero.

R-test

The models were also tested for lack of fit to determine whether they accurately described the data. This was done using a quantitative lack of fit test by calculating the ratio, R, where R is given by (29)

$$R = \frac{(SSR - v_2\sigma^2_{cp})/(n-p-v_2)}{\sigma^2_{c.p.}} \qquad (2.9)$$

where $\sigma^2_{c.p.}$ was the estimated variance at the centrepoints assuming the possible effect of pH or $[H^+]$ in this region was negligible and v_2 was the degrees of freedom associated with $\sigma^2_{c.p.}$. In using this test the variance estimates were not good estimates of the pure error variance since the pH varied from run to run. The values used were variances of the responses at the design centrepoint (see Table 2.5). However, the actual pure error variance would be a much smaller value. Any model which did not pass the lack of fit test with the variance estimate that was used, would not pass the lack of fit test with a better estimate of the pure error variance. The ratio, R, was compared with $F_{0.05,\ v_1,v_2}$ to determine whether a quantitative lack of fit was evident, (i.e. R greater than $F_{0.05,\ v_1,v_2}$). This was a significance test of the null hypothesis that the bias due to model inadequacy is zero (i.e. the error caused by lack of fit was not significantly greater that the pure error).

Table 2.5

Means and Variances of the Response Variables at the Design Centrepoint

Variable	Mean	σ^2
Filtercake Yield (g)	23.899	.324
Uranium Precipitated (g)	14.435	.149
Uranium Content of the Cake (wt%)	60.409	1.452
Barrens (g/l)	.0023	1.489×10^{-5}
Conversion (%)	98.440	1.457
Sulphur (wt%)	.216	.007
Mean Particle Size (μm)	8.884	7.094
Particle Size Distribution (Coefficient of Variation)	.388	.006

3. EXPERIMENTAL PROCEDURE

3.1 Introduction

The uranium source was a blend of scrap yellowcake from previous experimental investigations. The blended yellowcake was analyzed for uranium content which was found to be 67.86% U by weight.

The required amount of yellowcake for any given run was dissolved in the stoichiometric amount of sulphuric acid to form $UO_2 (SO_4)_3^{4-}$. The excess amount of H_2SO_4 required by the experimental design was also added at this stage. A small amount of distilled water was added to the solution to utilize the heat of reaction to facilitate in the dissolution of the uranium. After complete dissolution of the solids, the solution was transferred to a 1 litre volumetric flask and diluted with distilled water. The solution was then transferred to a 4 litre beaker and the mixer was started. The mixer used was a variable speed mixer with

a propellor type impeller having 1" blades. Magnesium oxide was added to raise the pH to approximately 3.0 followed by the rapid addition of the required experimental amount of 30% hydrogen peroxide. Magnesium oxide was then added to adjust the pH. The suspension was continually stirred at 175 rpm (stirrer Reynolds Number was approximately 1500) throughout the time of the run.

On the completion of the precipitation, the suspension was filtered through a Buchner funnel using Whatman 42 filter paper. The filtrate was sent to the analytical chemistry department at CANMET to determine the uranium in the barrens solution. The filtercake was air dried for two to three days then weighed on a Mettler balance to give the filtercake yield. The cake was then sent for analysis to determine the uranium, magnesium and sulphur contents of the cake.

3.2 pH Measurement

The pH was measured using a Fisher Accumet Model 420 pH/Ion Meter. For the experimental runs, the pH meter was calibrated using a buffer solution of pH 2.00 and the digestion pH was noted. After filtration, the pH of the solution was again measured by calibrating the pH meter using a pH standard closer to the noted pH. The pH determined at this point was considered to be the precipitation pH.

3.3 The Determination of the Uranium Values

The uranium contents of the cake and of the filtrate were determined by the analytical chemistry division of CANMET. The analytical method used was fluorimetry.

3.4 Particle Size Analysis

The particle size analyses of the samples were carried out using image analysis techniques by the Mineralogy Section of the Mineral Science Group. A small sample for each run was mounted upon a microscope slide in emulsion oil and placed under a microscope. An image of the field was transmitted to a computer

which performed the analysis. Eight to ten fields were analyzed for each sample. The resultant data were presented in terms of the percentage of the sample which would be retained by a sieve of the given size.

4. RESULTS AND DISCUSSION

4.1 Analysis of Results

The experimental results are given in Appendix A. Each set of data has been analyzed using least squares by fitting the data to linear equation, see Table 4.1 for range and variables studied

$$Y = \beta_0+\beta_1x_1+\beta_2x_2+\ldots + \beta_{12}x_1x_2++\beta_{13}x_1x_3 + \ldots$$
$$+ \beta_{45}x_4x_5 + \beta_{11}x_1^2 + \ldots \beta_{55}x_5^2 \qquad (4.1)$$

for the central composite design (Experimental Plan I) for each of the four cases discussed in Chapter 2. For the fractional factorial design with centrepoints (Plan II), the quadratic effects were dropped from equation 4.1 (e.g. $\beta_{11}x_1^2$ to $B_{55}x_5^2$), hence, only the main effects and 2 variable interaction effects were analyzed. Only cases 1 and 3 were used for this analysis. The resultant parameter values from the least squares analysis of equation 4.1 were evaluated for their significance by calculating their 80, 90 and 95% confidence intervals.

4.2 Filtercake Yield

The models describing filtercake yield and the results of the statistical test for Experimental Plan I have been given in Table 4.2. The resultant parameters indicated that the filtercake yield was affected by the initial uranium content, the amount of hydrogen peroxide added, and the pH. The results of the R-test indicate that none of the models adequately represented the data. This was confirmed by Figures 4.1 through 4.3 in which there is no real evidence of a

Table 4.1

Range of Operating Variables Studied

Symbol	Variable	Range
X_1	Initial Uranium Concentration (g/l)	10 - 20
X_2	Mol Ratio 4: H_2O_2	0.75 - 3.75
X_2*	Peroxide Concentration g/l	2.68 - 4.82
X_3	pH	2.4 - 4.8
X_3*	Hydrogen Concentration g mol/l	1.478×10^{-3} 5.823×10^{-6}
X_5	Excess Sulphate g/l	0 - 17.6
X_5*	Total Sulphate g/l	19.34 - 27.37
X_5	Time hours	1.0 - 5.0

Table 4.2

Plausible Models for the Filtercake Yield for Experimental Plan I

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	24.126± .658	79.988	2.50
		β_1	3.916± .658		
		β_2	1.150± .658		
		β_{22}	-1.019± .658		
2/1	95	β_0	23.40	517.904	14.979
2/2	80,90	β_0	24.126± .765	111.705	3.39
		β_1	3.916± .765		
		β_{22}	-1.091± .765		
3/1	all	β_0	24.009± .707	91.680	2.865
		β_1	3.426± .788		
		β_2*	2.603±1.410		
		β_{22}*	2.885±1.945		
4/1	80	β_0	23.991± .788	113.262	3.539
		β_1	4.191± .802		
		β_3*	-1.819±1.605		
		β_{22}*	-2.803±2.177		
4/2	90,95	β_0	23.895± .832	132.140	4.004
		β_1	4.046± .841		
		β_{22}*	-2.345±2.272		

Table 4.2 (Cont'd)

Q-test Results				R-test Results		
Model A	Model B	Q	F	Case/Model	R	F
2/1	2/2	60.0	3.30	1/1	10.36	2.91
4/2	4/1	5.33	4.15	2/2	14.01	2.90
				3/1	11.91	2.91
				4/1	14.81	2.91

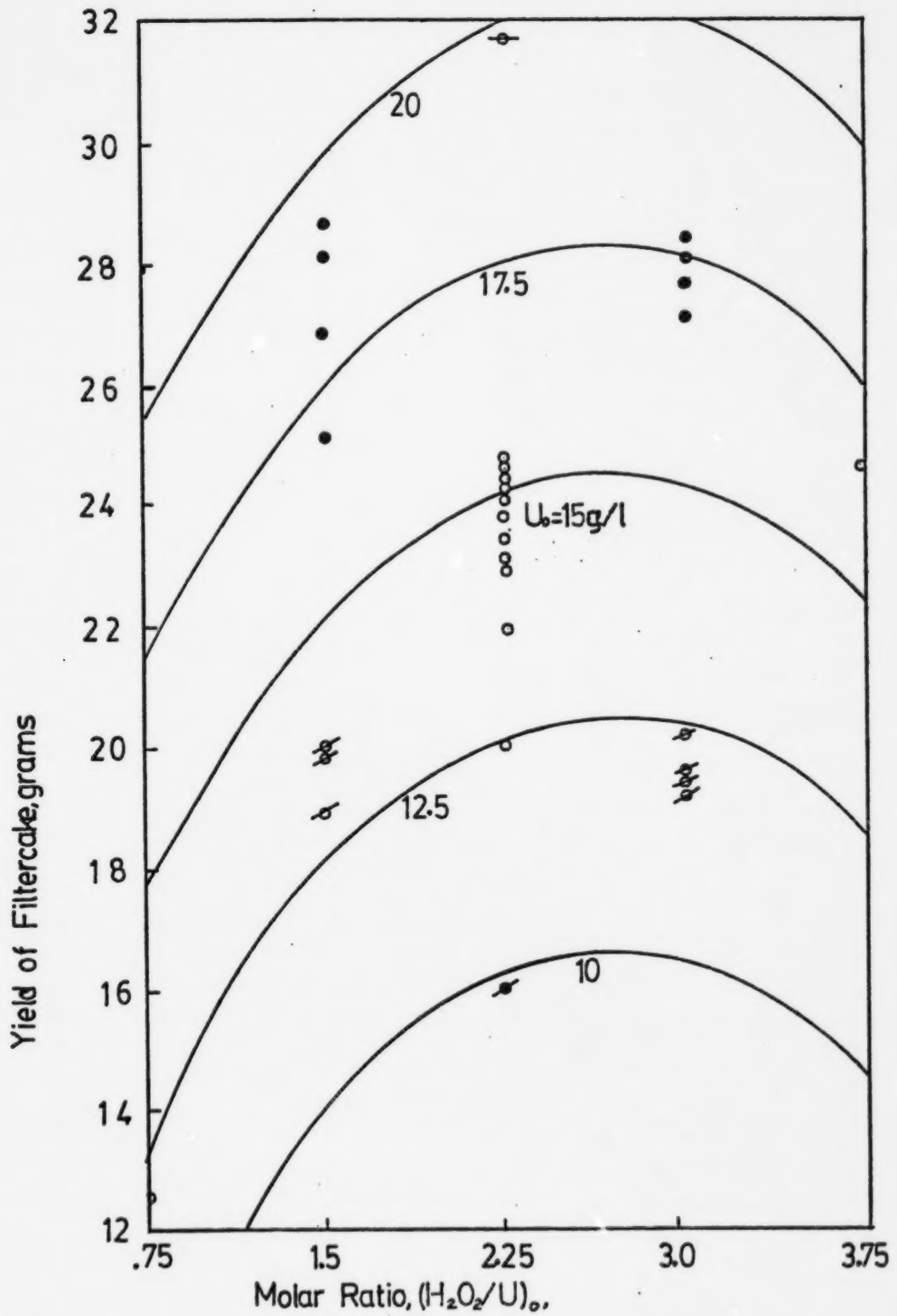

Figure 4.1: Resultant Model for Filtercake Yield for Plan I - Model 1/1
(⊖ - U_0=20g/l, ● -U_0=17.5g/l, o-U_0=15g/l, ⊘-U_0=12.5g/l, ⊘-U_0=10g/l)

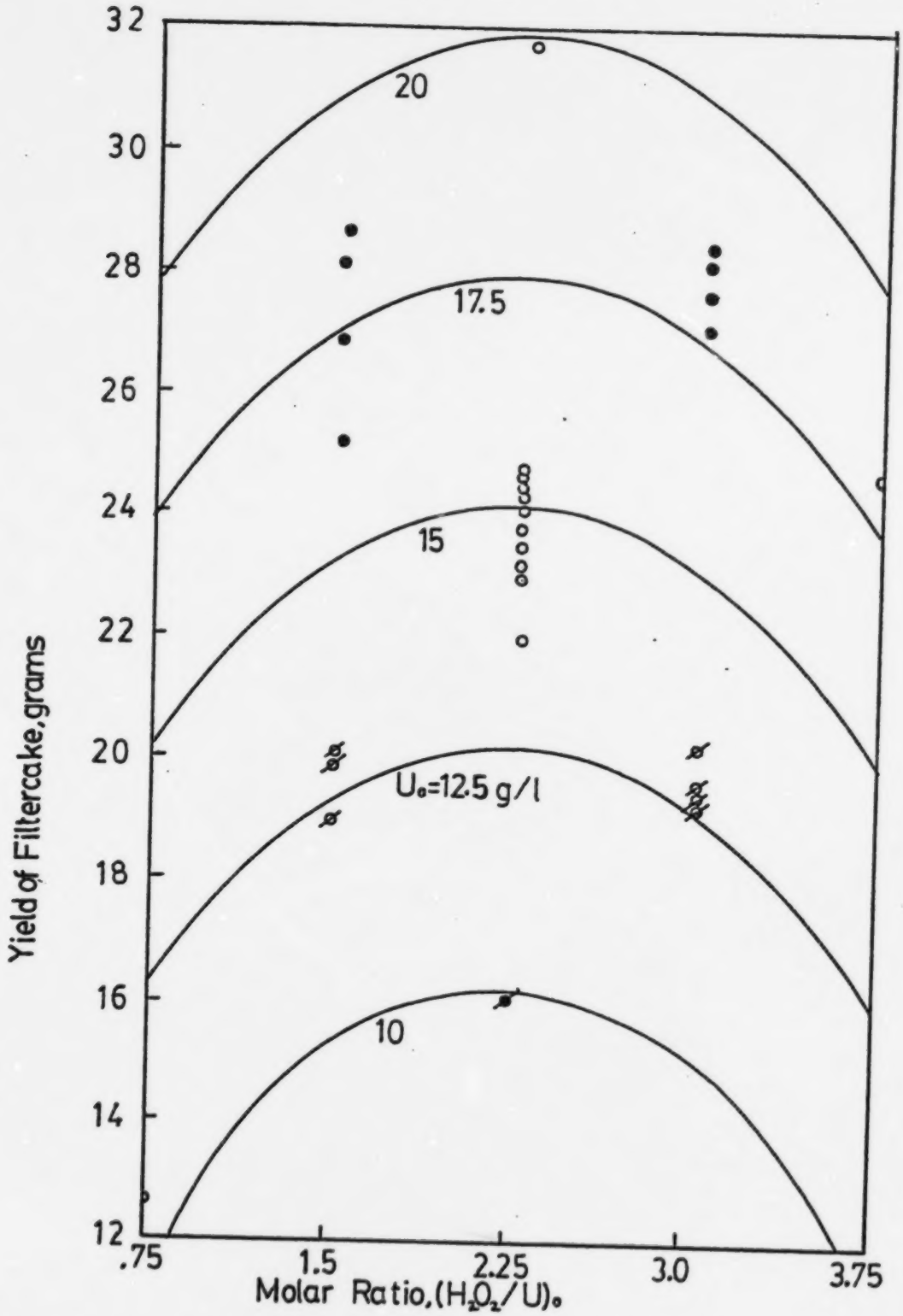

Figure 4.2: Resultant Model for Filtercake Yield for Płan I - Model 2/2
(Refer to Figure 4.1 for the Legend)

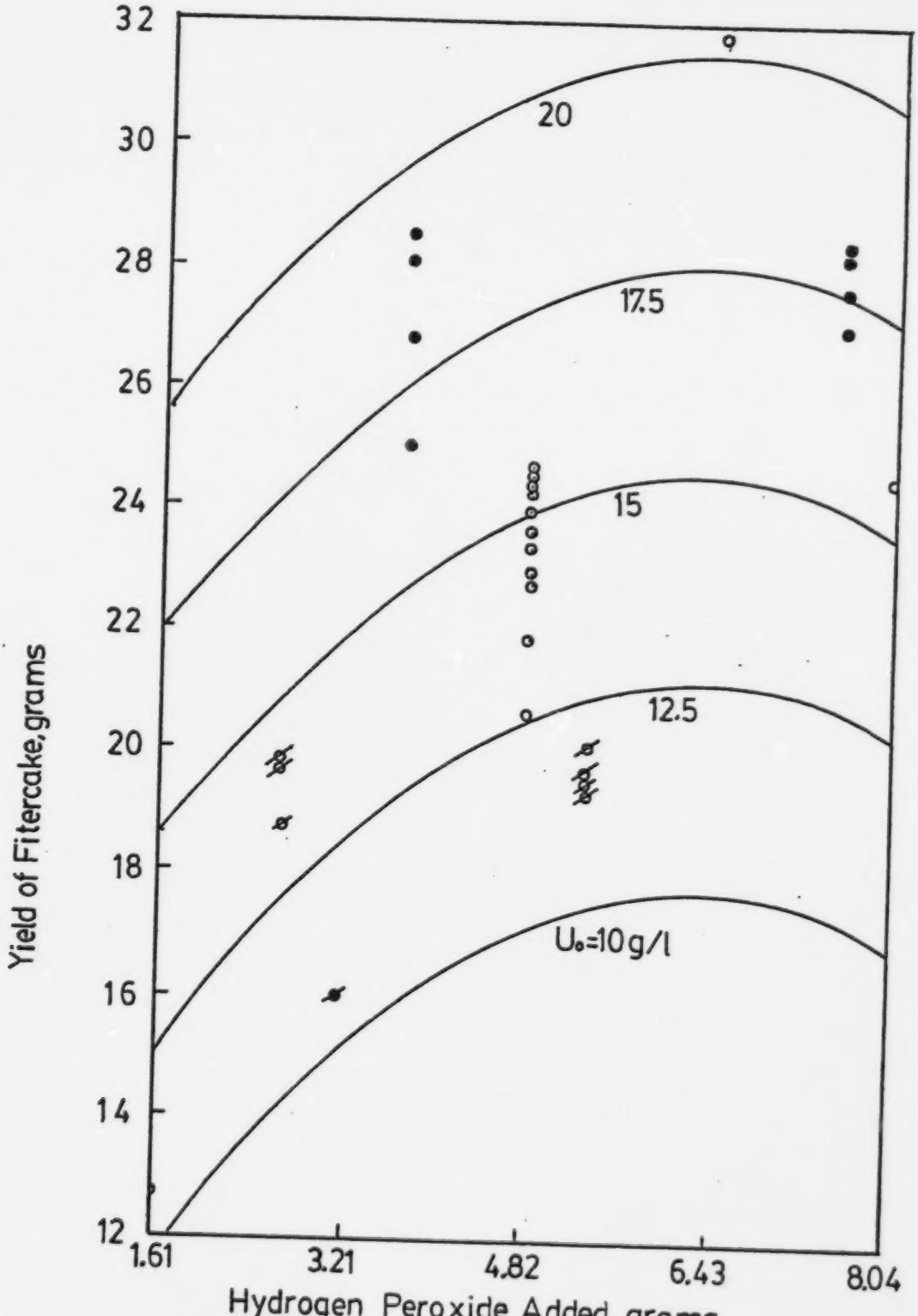

Figure 4.3: Resultant Model for Filtercake Yield for Plan I - Model 3/1
(Refer to Figure 4.1 for the Legend)

quadratic effect of the hydrogen peroxide content. The source of this lack of fit was determined to be Run 19 at which point, the peroxide level was below the stoichiometric amount. Exclusion of this run and evaluating the effect of only the initial uranium content of the solution indicated that the data could be well represented as only a function of the initial uranium content provided that sufficient hydrogen peroxide is added to the solution.

The results of Experimental Plan II, given Table 4.3, also indicated that the filtercake yield was again mainly a function of the initial uranium content. However, the pH was also found to be significant. A possible effect of the amount of peroxide added was noted. Figures 4.5 and 4.6 illustrate the linear dependency of the filtercake yield upon initial uranium content and pH.

4.3 Uranium Precipitated

The amount of uranium precipitated for a given run was determined by multiplying the filtercake yield by the uranium content of the cake for the run. All of the models for Experimental Plan I given in Table 4.4 demonstrated lack of fit. The model for Case 3 (Model 3/1) has been plotted and presented in Figure 4.7. This plot clearly demonstrates the effect of Run 19 in causing the lack of fit. The plot indicated that the amount of uranium precipitated was clearly proportional to the initial amount of uranium in solution. However, because of the large residual amount between Run 19 and the curve, the quantitative lack of fit test failed. It should be noted that the values of the parameters were similar to those given for Model 3/1 in Table 4.5. It should also be noted that although pH affected the filtercake yield, it was not a significant parameter for the amount of uranium precipitated.

Figures 4.8 through 4.10 illustrate that the quadratic effect indicated by Run 19 does not in fact exist. As can be seen by these figures, the fitting routine in trying to minimize the residual of Run 19 has caused the resultant

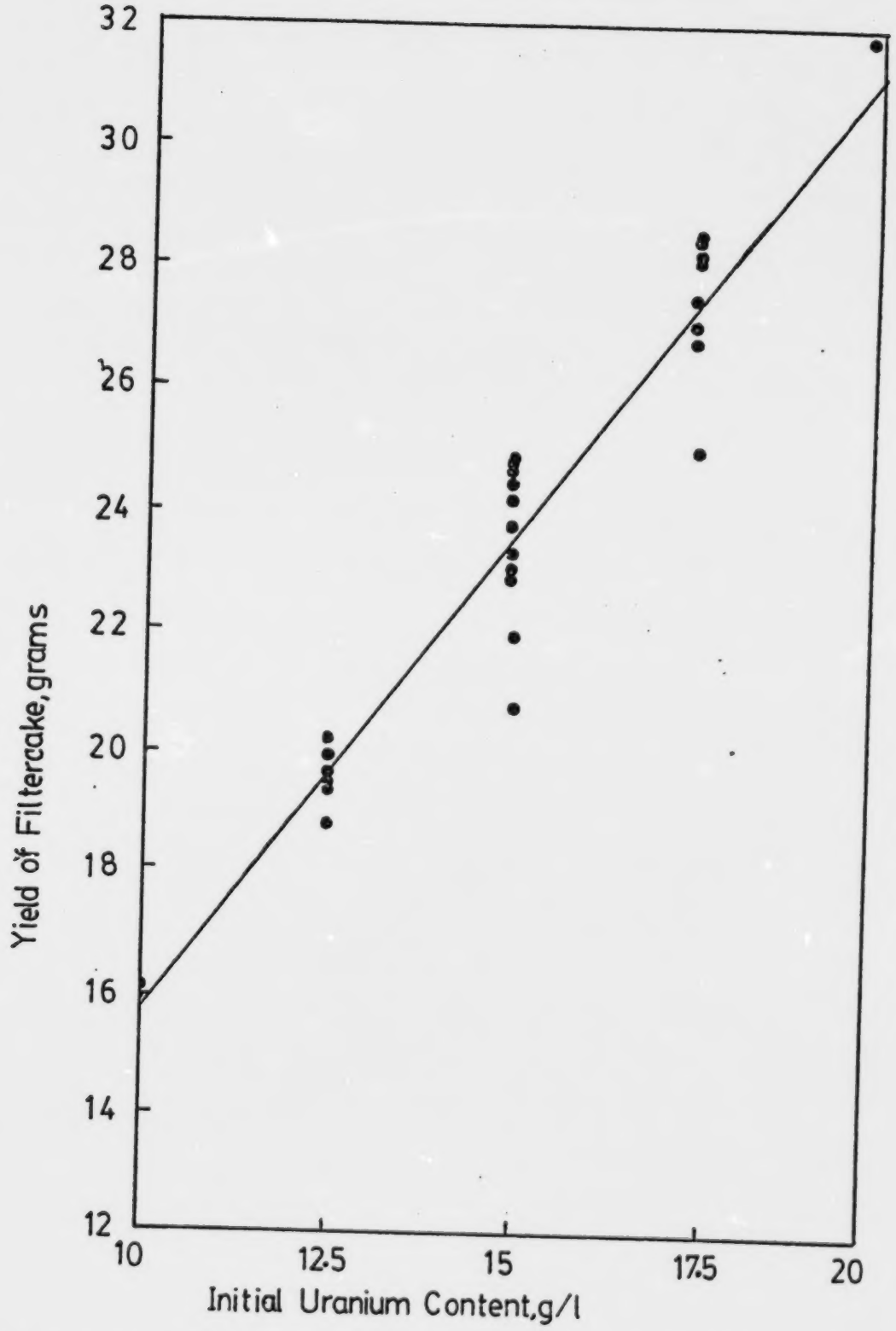

Figure 4.4: Effect of Initial Uranium Concentration upon the Filtercake Yield Excluding Run Number 19.

Table 4.3

Plausible Models for the Filtercake Yield for Experimental Plan II

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	90	β_0	23.717±.317	14.739	.614
		β_1	3.903±.404		
1/2	95	β_0	23.731±.276	10.66	.463
		β_1	3.915±.352		
		β_3	.777±.529		
3/1	90	β_0	23.711±.257	8.774	.399
		β_1	3.911±.335		
		β_2*	.347±.335		
		β_3	.873±.504		
3/2	95	β_0	23.717±.317	14.739	.614
		β_1	3.903±.404		

Q-test Results

Model A	Model B	Q	F
1/1	1/2	8.81	4.28
3/2	3/1	7.47	3.40

R-Test Results

Case/Model	R	F
1/2	1.71	3.02
3/1	1.39	3.04

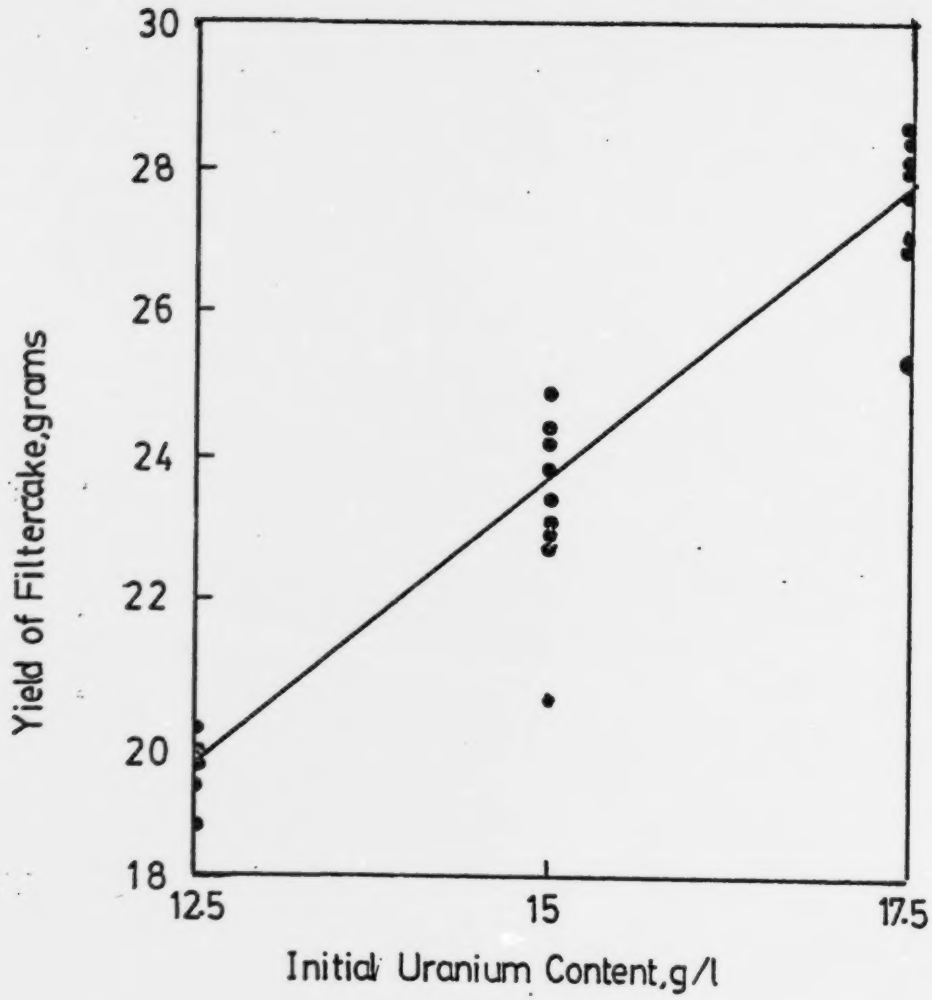

Figure 4.5: Effect of Initial Uranium Concentration upon the Filtercake Yield for Plan II - Model 1/1

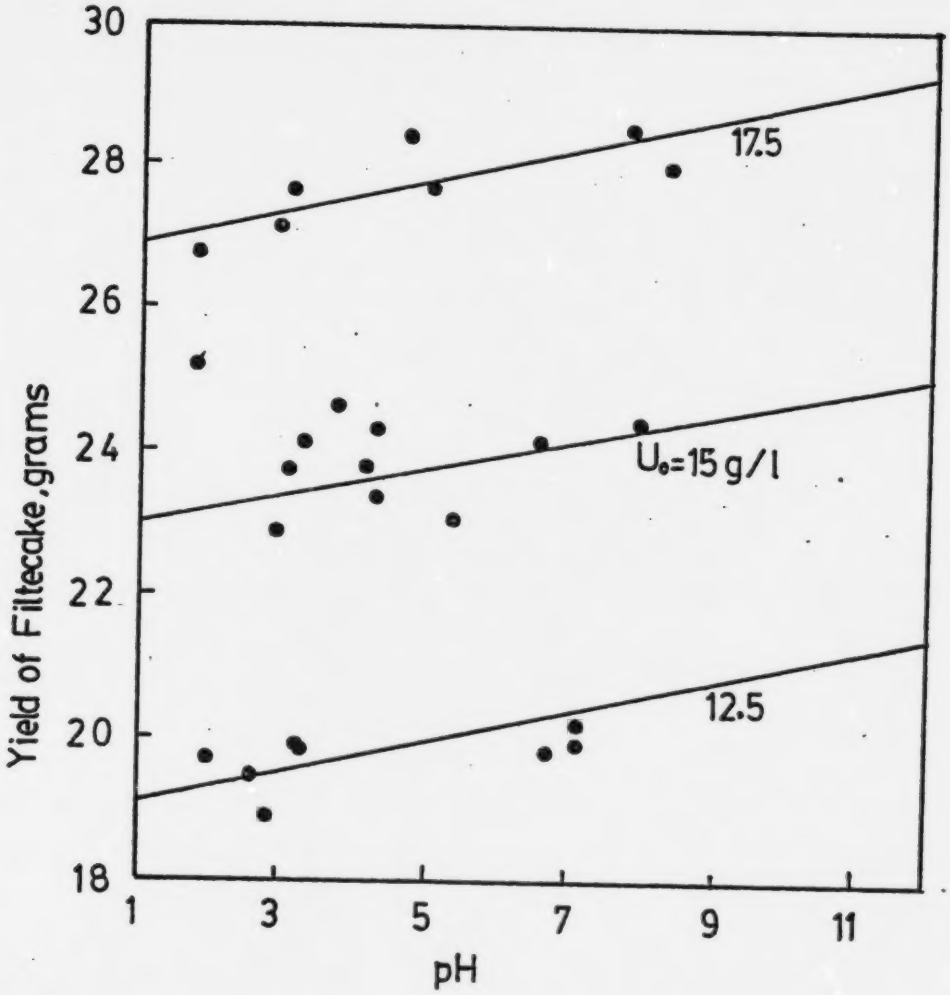

Figure 4.6: Resultant Model for Filtercake Yield for Plan II - Model 1/2

Table 4.4

Plausible Models for the Uranium Precipitated for Experimental Plan I

Case/ Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	14.033± .420	52.216	1.536
		β_1	2.408± .515		
2/1	80	β_0	14.513± .432	35.601	1.079
		β_1	2.407± .432		
		β_{22}	- .721± .392		
2/2	90,95	β_0	14.033	179.820	5.138
3/1	80	β_0	14.441± .354	22.198	.716
		β_1	2.179± .400		
		β_2*	1.534± .716		
		β_{12}*	1.106± .868		
		β_{22}*	- 2.805±1.181		
3/2	90,95	β_0	14.445± .384	27.037	.845
		β_1	2.095± .428		
		β_2*	1.683± .767		
		β_{22}*	1.953±1.057		
4/1	80	β_0	14.374± .441	35.890	1.216
		β_1	2.559± .428		
		β_{12}*	1.408±1.071		
		β_{22}*	- 2.728±1.476		

Table 4.4 (Cont'd)

Case/ Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
4/2	90,95	β_0	14.371± .480	43.951	1.332
		β_1	2.496± .485		
		β_{22}*	- 1.604±1.311		

Q-test Results

Model A	Model B	Q	F
2/2	2/1	66.84	3.29
3/2	3/1	6.76	4.16
4/2	4/1	6.63	4.14

R-test Results

Case/Model	R	F
1/1	13.66	2.89
2/1	9.58	2.90
3/1	7.84	2.92
4/1	10.08	2.91

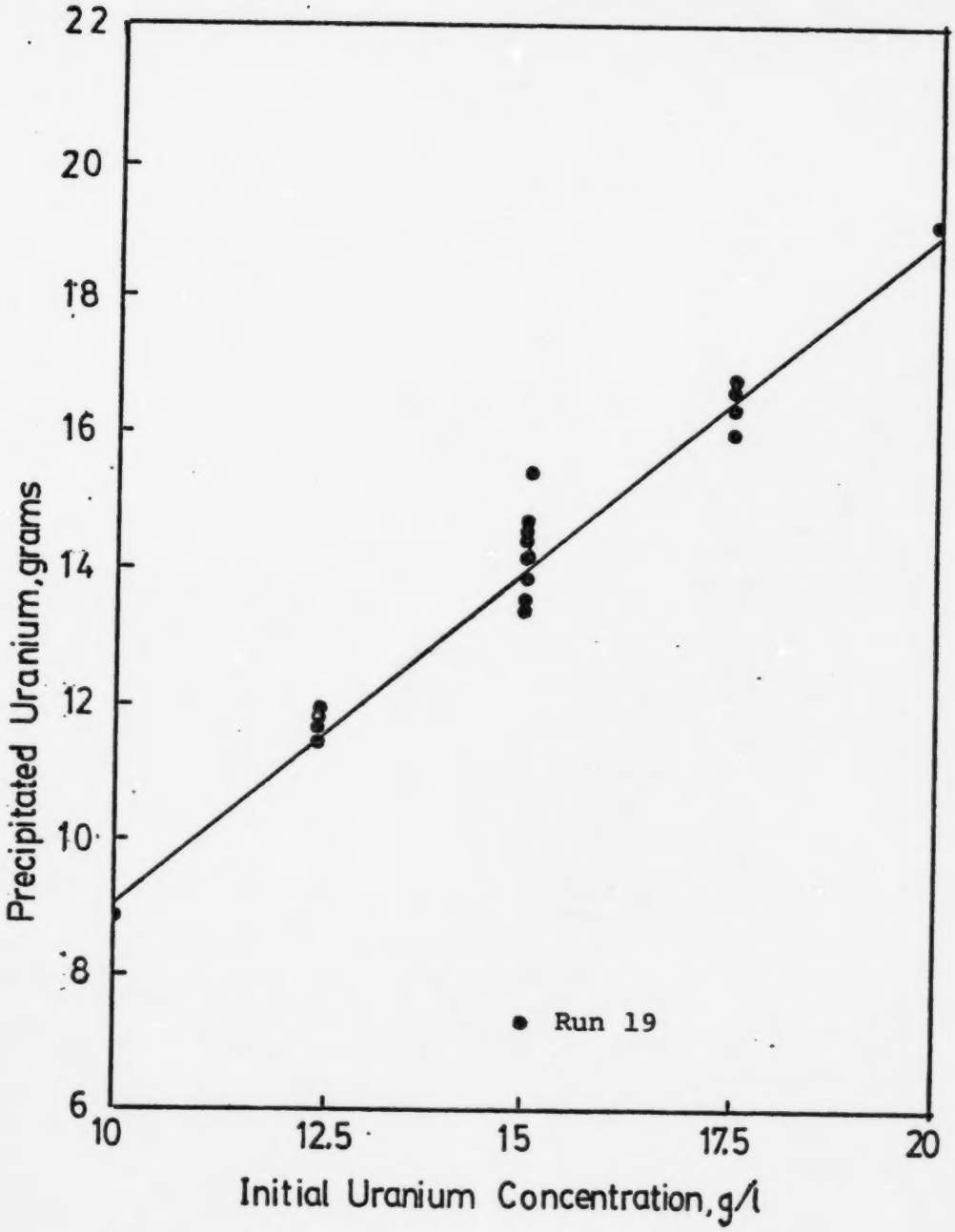

Figure 4.7: Resultant Model for the Amount of Uranium Precipitated for Plan I - Model 1/1

Table 4.5

Plausible Models for the Uranium Precipitated for Experimental Plan II

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	14.245± .170	4.703	.196
		β_1	2.327± .216		
3/1	all	β_0	14.319± .192	3.257	.148
		β_1	2.327± .218		
		β_{14}*	- .533± .437		
		β_{24}*	.760± .705		

Q-Test Results

Model A	Model B	Q	F
1/1	3/1	9.77	4.20

R-test Results

Case/Model	R	F
1/1	1.50	3.01
3/1	0.99	3.06

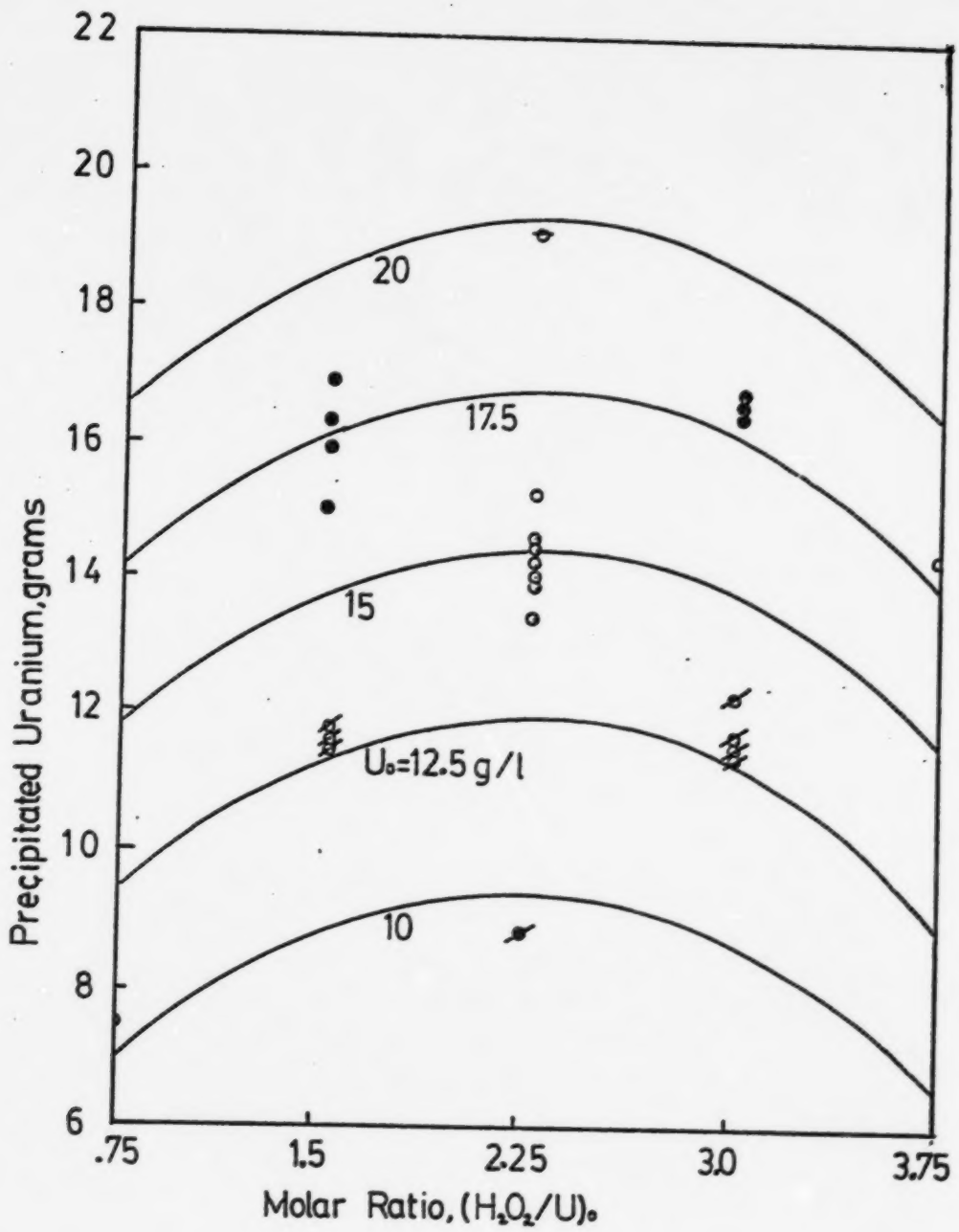

Figure 4.8: Resultant Model for the Amount of Uranium Precipitated for Plan I - Model 2/1

(Refer to Figure 4.1 for the Legend)

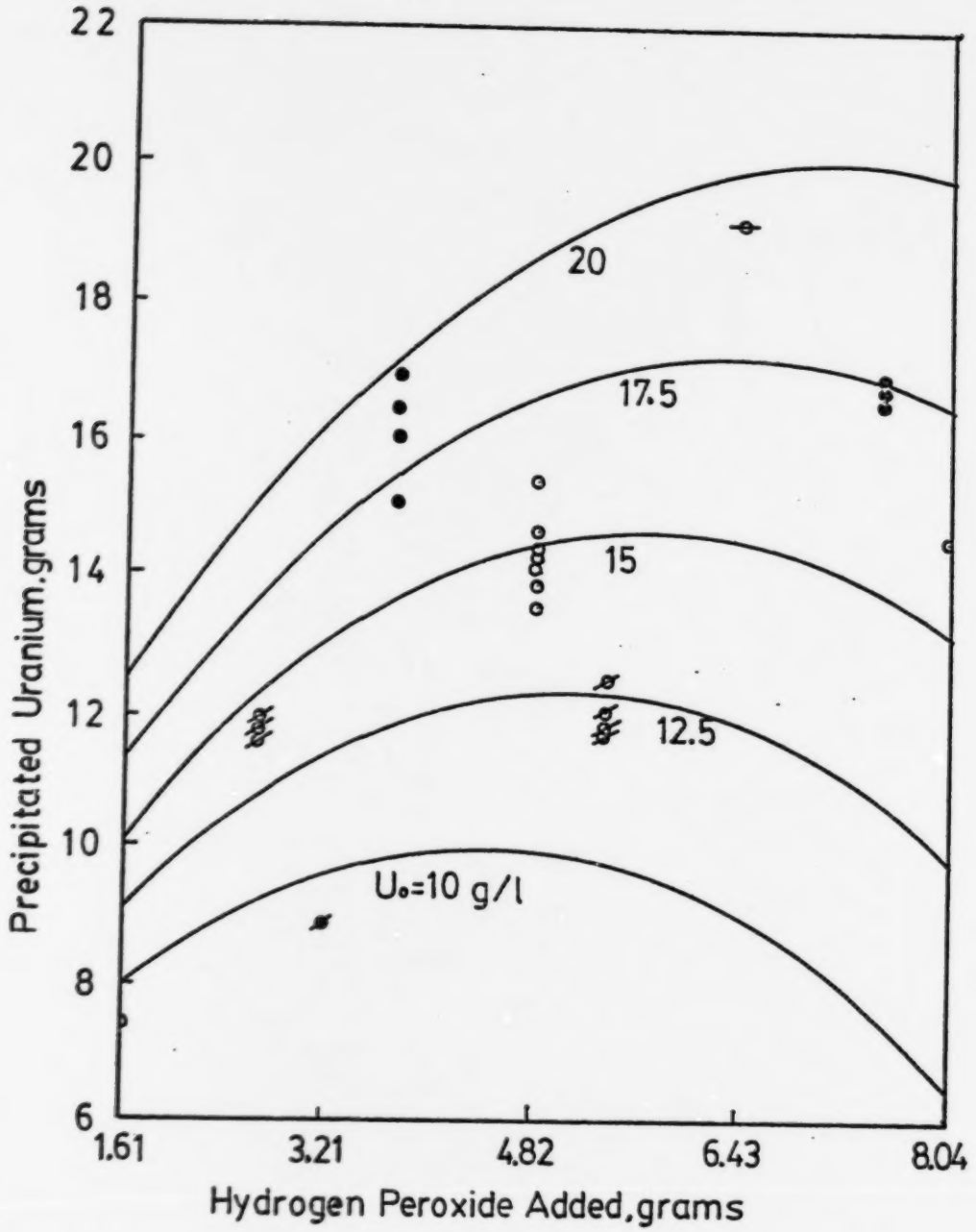

Figure 4.9: Resultant Model for the Amount of Uranium Precipitated for Plan I - Model 3/1

(Refer to Figure 4.1 for the Legend)

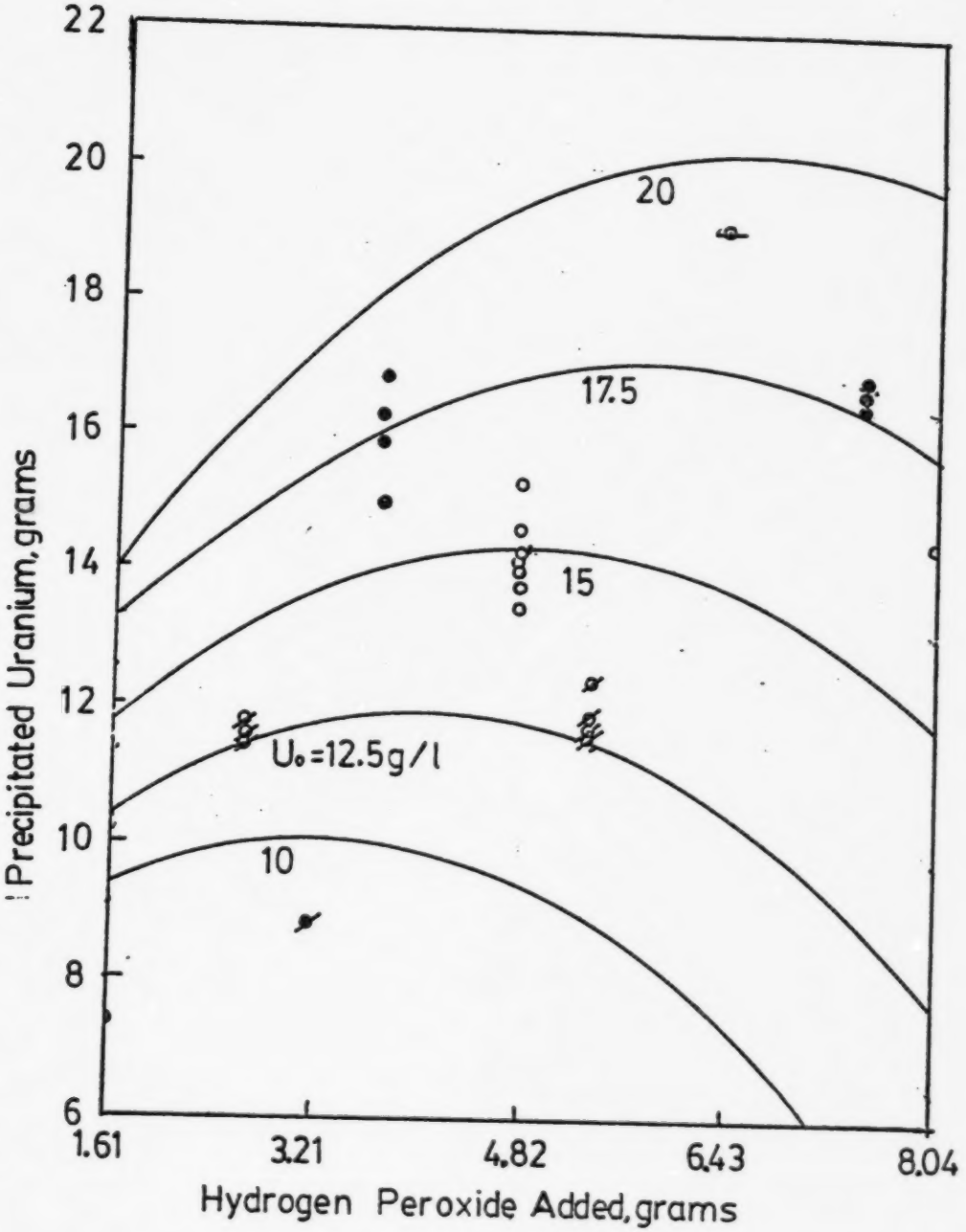

Figure 4.10: Resultant Model for the Amount of Uranium Precipitated for Plan I - Model 4/1

(Refer to Figure 4.1 for the Legend)

curves to unacceptably fit the rest of the data.

The results for Experimental Plan II are given in Table 4.5. Model 3/1 has been plotted in Figure 4.11. As may be seen from this plot, the uranium precipitated is proportional to the initial amount of uranium in solution and was well represented by this case. However, Model 3/1 indicated that the sulphate level and the amount of hydrogen peroxide added also contributed to the amount of uranium precipitated. The signs of the parameters for β_{14}* and β_{24}* may be interpreted as follows. The value of β_{24}* indicated that with increasing sulphate level, more peroxide should be added to obtain the highest amount of uranium. The value of β_{14}* indicated that as the amount of sulphate is increased the amount uranium that will be precipitated will decrease, hence, the precipitation process should be run with as low a sulphate level as is feasible.

4.4 Barrens Concentration

None of the models presented in Tables. 4.6 and 4.7 to represent the uranium concentration of the barrens passed the lack of fit test. The reason for this was that the data were spread over several orders of magnitude (e.g. for point 10, the concentration of uranium in the barrens was 1.57 g/l while for point 31, the concentration was less than .0001 g/l). Because of this large variation, the data were forced through the large values of concentration causing the fit to be poor for the smaller values. In fact, the values of the residuals for most points were larger than the concentration values (i.e. the error was larger than the actual value). By plotting the log of the barrens concentration vs pH (Figure 4.12) a linear trend was observed indicating a pH dependence for the uranium left in solution after the reaction. It is interesting to note that this pH dependence apparently did not appear when examining the amount of uranium precipitated. This may be explained by noting that although the differences between the concentration of uranium in the barrens are relatively large when

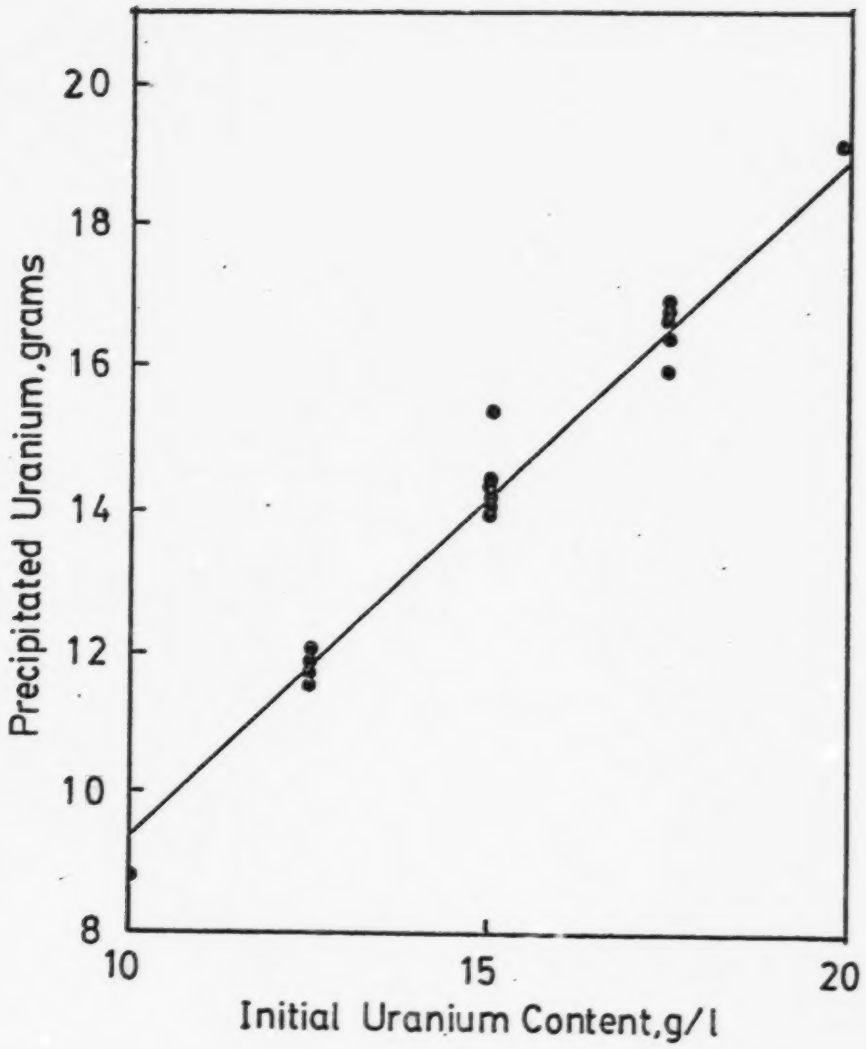

Figure 4.11: Resultant Model for the Amount of Uranium Precipitated for Plan II - Model I/1

Table 4.6

Plausible Models for the Barrens Concentration for Experimental Plan I

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Paramater Values	SSR	$\hat{\sigma}^2$
1/1	all	β_2	- .586± .301	17.910	.527
		β_{22}	- .764± .213		
2/1	all	β_{22}	.764± .270	29.582	.845
3/1	80,90	β_2*	- 1.004± .549	17.640	.535
		β_{12}*	- 1.230± .738		
		β_{22}*	2.505± .875		
3/2	95	β_2*	- 1.906± .625	23.802	.700
		β_{22}*	1.560± .780		
4/1	80	β_{12}*	- 1.365± .861	25.036	.736
		β_{22}*	- 2.405±1.038		
4/2	90,95	β_{22}*	1.337± .888	32.694	.934

Q-test Results

Model A	Model B	Q	F
3/2	3/1	11.53	4.14
4/2	4/1	10.40	4.13

R-test Results

Case/Model	R	F
1/1	311.12	2.90
2/1	494.34	2.91
3/1	319.19	2.90
4/1	435.05	2.91

Table 4.7

Plausible Models for the Barrens Concentration
For Experimental Plan II

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	90	β_2	- .175± .132	1.316	.060
		β_3	- .306± .301		
		β_{24}	- .153± .132		
		β_{34}	- .292± .215		
1/2	95	β_0	.109± .100	1.210	.058
		β_2	- .131± .126		
		β_{12}	- .179± .132		
		β_{24}	- .135± .129		
		β_{35}	.363± .223		

R-test Results

Case/Model	R	F
1/1	43.32	3.06
1/2	43.09	3.07

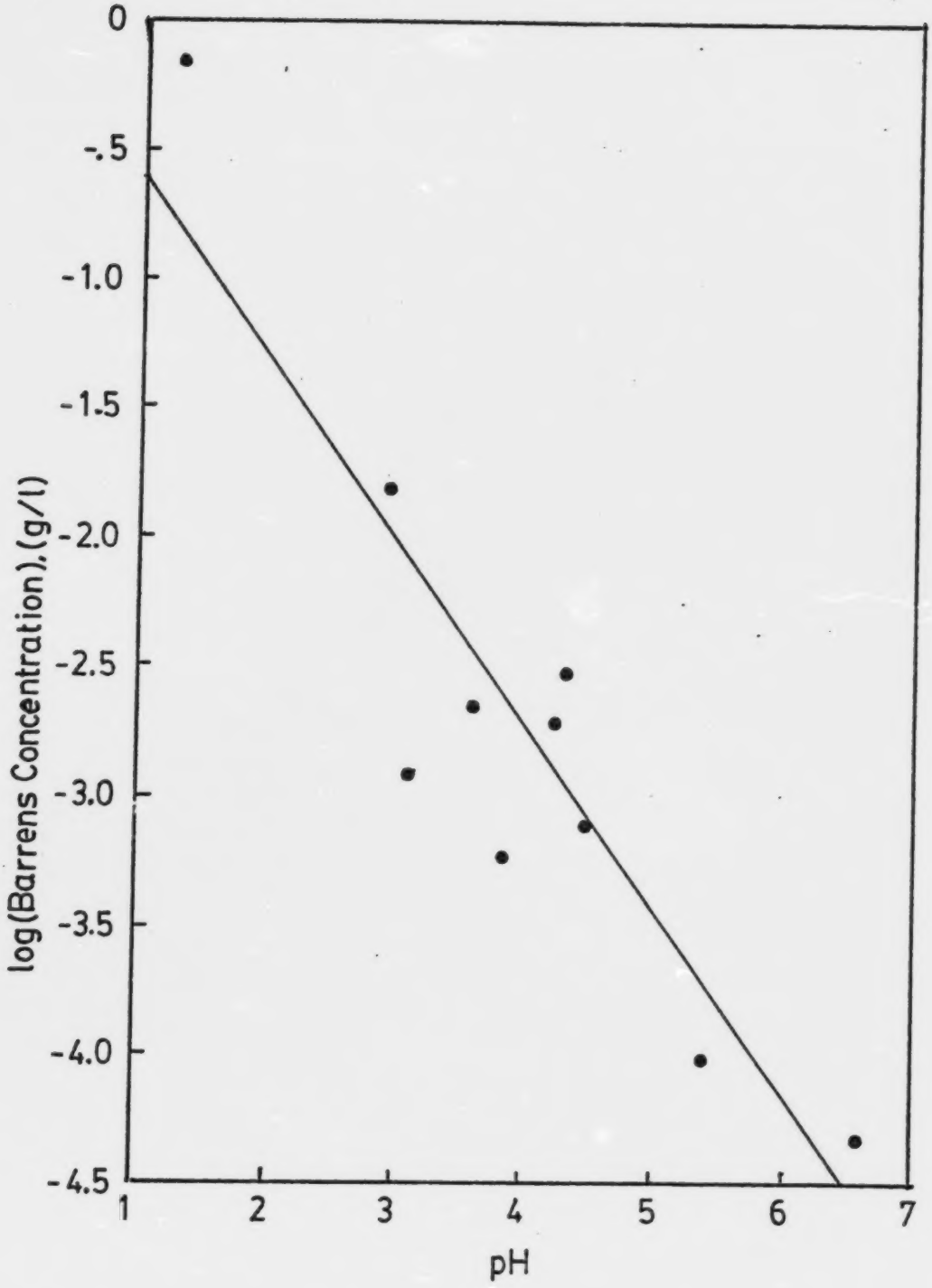

Figure 4.12: The Effect of pH upon the Barrens Concentration at the Centrepoint

compared to each other they are relatively small when compared to the amount of uranium precipitated.

By comparing the values of the parameters given in Table 4.7 with those of Table 4.5 it may be seen that in general, the significant variables affected the barrens concentration in the opposite way to that of the amount of uranium precipitated. This would be expected if one considers a mass-balance. Although the results obtained in testing the models for the barrens concentration all showed a lack of fit, it does appear that the barrens concentration is sensitive to the precipitation pH and possibly time; variables which were relatively insignificant when modelling the amount of uranium precipitated. Due to this large range of barrens concentrations these effects should be evaluated using techniques such as non-linear modelling.

4.5. Conversion

Conversion was calculated by dividing the amount of uranium precipitated by the initial amount of uranium added to the solution. All of the models in Tables 4.8 and 4.9 failed the lack of fit test, although Model 3/1 in Table 4.9 demonstrated a barely significant lack of fit. Hence, it is quite possible that conversion is affected by the initial uranium content, the amount of peroxide added and the sulphur content of the solution. The results indicated that the conversion could be expected to be quite high (in the range of 95-100%) over the entire range of the operating variables. The only exceptions were for runs 10 and 19 in which the conversions were significantly lower. Examination of the operating variables for these runs indicated that in both instances, the amount of peroxide added was small relative to the amount of sulphate added (i.e. lowest amounts of peroxide and high amounts of sulphate. In the case of run 10 the pH was also quite low. Comparing the results of run 10 with those of run 14 which was run at a significantly higher pH all other variables the same indicated a possible pH

Table 4.8

Plausible Models for Conversion
for Experimental Plan I

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	99.267±2.086	831.306	25.191
		β_2	4.337±2.086		
		β_{22}	4.708±1.806		
2/1	all	β_0	99.267±2.550	1282.666	37.255
		β_{22}	- 4.708±2.208		
3/1	80	β_0	98.853±2.148	847.576	26.487
		β_2*	8.134±3.900		
		β_{12}*	7.526±5.200		
		β_{22}*	-18.818±7.097		
3/2	90,95	β_0	98.902±2.383	1077.981	32.666
		β_2*	8.703±4.304		
		β_{22}*	-13.120±6.550		
4/1	80	β_0	98.328±2.625	1326.090	40.185
		β_{12}*	8.620±6.366		
		β_{22}*	-17.198±8.680		
4/2	90,95	β_0	98.343±2.866	1631.479	47.985
		β_{22}*	-10.473±7.771		

Q-test Results

Model A	Model B	Q	F
3/2	3/1	8.70	4.15
4/2	4/1	7.60	4.14

R-test Results

Case-Model	R	F
1/1	23.40	2.90
2/1	34.84	2.89
3/1	24.90	2.91
4/1	37.55	2.90

Table 4.9

Plausible Models for Conversion
for Experimental Plan II

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	97.401	108.440	4.338
3/1	all	β_0	97.857± .824	75.586	3.286
		β_{14}*	2.261±1.879		
		β_{24}*	3.540±3.028		

R-test Results

Case/Model	R	F
1/1	4.09	3.00
3/1	3.06	3.02

effect. As a result an increase in operating pH may be necessary if initial sulphate concentrations are high. Clearly, more study is needed in this area to fully investigate the interaction between sulphate and peroxide.

4.6 Uranium Content

The only variable of note to affect the uranium content of the cake was the pH. As may be seen in Tables 4.10 and 4.11 and illustrated in Figure 4.13 the uranium content of the cake decreased as the pH was increased. It should be noted that the cakes in question were not dried by standard methods but were air dried to constant weight. Therefore, some residual moisture may be present in the cakes. Assuming however that the residual moisture is randomly distributed from cake to cake, then it should not affect the results. Also, the chemical formula $UO_4.2H_2O$ contains hydrated water which may also be removed from drying. Excluding this hydrated water, the cakes in actual fact have purities in the range of 88 to 100% U_3O_8.

In any further studies, in order to verify the pH affect it is recommended that the cakes be properly dried. In this study it was not carried out in order that the particle sizes would not be affected by the drying procedure causing possible caking effects.

4.7 Sulphur Content

As may be seen from Tables 4.12 and 4.13, the sulphur content of the cake was dependent upon all of the variables in one form or another. The reason for measuring the sulphur content was to determine whether at lower peroxide levels, the uranium would complex with the sulphur as is the case with ammonia precipitation. The results did indicate that at lower peroxide additions the sulphate levels increased, but not dramatically. Overall, the sulphate levels were well within refiners' specifications. Of particular interest in the modelling aspect of the sulphur content was the variation among the models. The resultant signi-

Table 4.10

Plausible Models for the Uranium Content of the Filtercake for Experimental Plan I

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	59.954± .468	64.972	1.911
		β_3	- 2.186± .833		
2/1	all	β_0	59.950±	114.603	3.274
3/1	all	β_0	59.954± .468	64.972	1.911
		β_3	- 2.186± .833		
4/1	80	β_0	60.322± .611	71.295	2.160
		β_3*	2.346±1.219		
		β_{11}	- .543± .529		
4/2	90,95	β_0	59.950	114.603	3.274

Q-test Results

Model A	Model B	Q	F
4/2	4/1	10.02	3.29

R-test Results

Case/Model	R	F
1/1	2.38	3.01
2/1	4.37	3.00
3/1	2.38	3.01
4/1	2.86	3.02

Table 4.11

Plausible Models for the Uranium Content of the Filtercake for Experimental Plan II

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	60.096± .439	27.705	1.154
		β_3	- 1.703± .833		
3/1	90	β_0	60.096± .439	27.705	1.154
		β_3	- 1.703± .833		
3/2	95	β_0	60.096	48.130	4.203

Q-test Results

Model A	Model B	Q	F
3/2	3/1	17.20	4.26

R-test Results

Case/Model	R	F
1/1	0.672	3.01
3/1	0.672	3.01

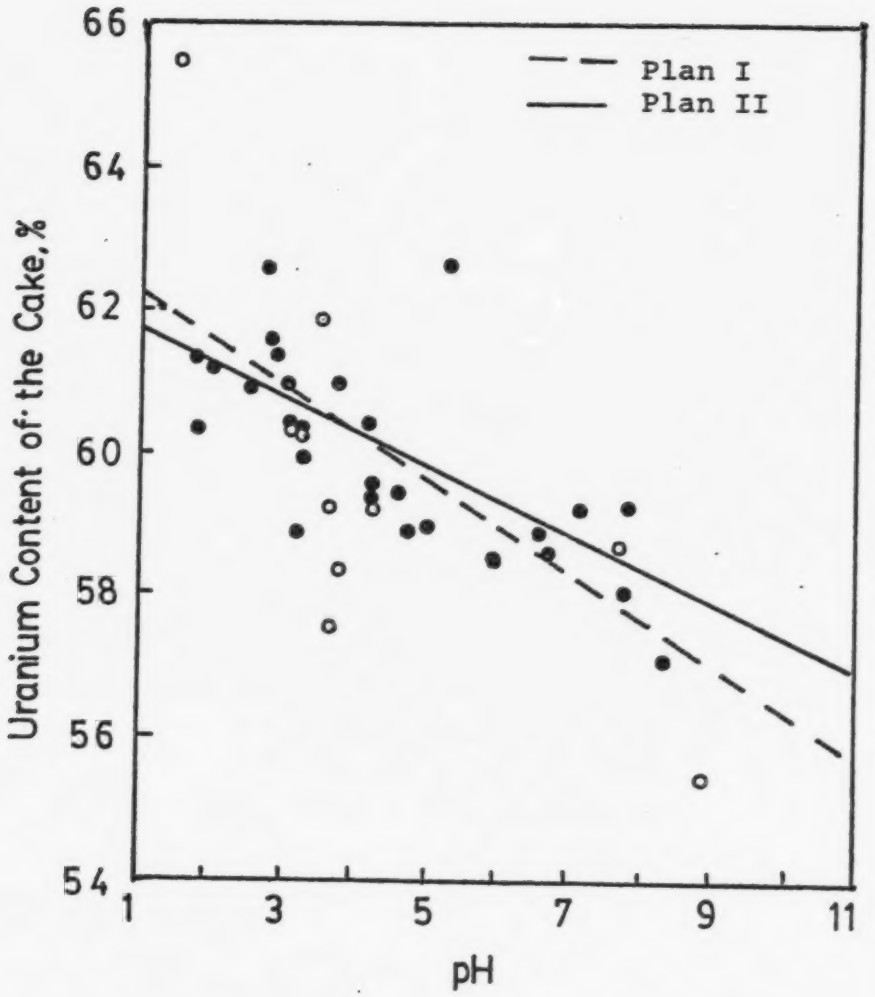

Figure 4.13 : The Effect of pH upon the Uranium Content of the Cake
(●- Factorial Design and Centrepoints
o- Added Central Composite Design Points)

Table 4.12

Plausible Models for the Sulphur Content of the Cake for Experimental Plan I

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	.240± .055	.365	.012
		β_2	- .065± .046		
		β_{24}	- .105± .056		
		β_{33}	- .134± .105		
		β_{55}	.059± .039		
2/1	all	β_0	.240± .046	.625	.018
		β_{24}	- .097± .069		
3/1	80	β_0	.231± .053	.204	.008
		β_2*	- .144± .075		
		β_4*	.094± .069		
		β_5	- .039± .036		
		β_{14}*	.145± .093		
		β_{24}*	- .420± .168		
		β_{34}*	- .110± .108		
		β_{45}*	- .090± .078		
		β_{22}	.120± .112		
		β_{33}	- .235± .111		
		β_{55}	.058± .033		
3/2	90	β_0	.250± .059	.388	.013
		β_2*	- .107± .091		
		β_{14}*	.157± .114		
		β_{24}*	- .345± .199		

Table 4.12 (Cont'd)

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
		β_{33}	- .225± .135		
		β_{55}	.058± .041		
3/3	95	β_0	.212± .028	.578	.018
		β_{24}*	- .201± .189		
		β_{55}	.060± .047		
4/1	80	β_0	.200± .058	.659	.019
		β_{55}	.060± .050		
4/2	90,95	β_0	.212± .028	.578	.018
		β_{24}*	- .201± .189		
		β_{55}	.060± .047		

Q-test Results

Model A	Model B	Q	F
3/3	3/2	4.91	2.53
3/2	3/1	4.51	2.60
4/1	4/2	4.67	4.15

R-test Results

Case/Model	R	F
1/1	1.96	2.92
2/1	3.21	2.89
3/1	1.26	3.00
4/2	3.07	2.90

Table 4.13

Plausible Models for the Sulphur Content of the Cake for Experimental Plan II

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	90	β_0	.236± .029	.098	.005
		β_2	- .049± .035		
		β_4	.053± .035		
		β_{24}	.097± .035		
		β_{45}	- .145± .035		
1/2	95	β_0	.236± .029	.195	.009
		β_2	- .049± .035		
		β_4	.053± .035		
		β_{24}	.097± .035		
3/1	all	β_0	.299± .046	.230	.011
		β_2*	- .118± .104		
		β_4*	.095± .093		
		β_{12}*	.149± .127		
		β_{24}*	- .294± .193		

Q-test Results

Model A	Model B	Q	F
1/2	1/1	19.4	4.32

R-test Results

Case/Model	R	F
1/1	0.42	3.07
3/1	1.99	3.07

ficant parameters for the cases indicated the need to consider more than the initial 95% confidence interval. The variation of the models between cases also indicated that the form or representation of the operating variables could have an effect upon which variables may be deemed significant. In light of the other results, it would seem that Case 3 was the best representation of the operating variables (i.e. use total sulphate rather than excess sulphate, amount of peroxide added rather than the H_2O_2/U molar ratio, and pH rather than H^+).

4.8 Size and Size Distribution

The mean size and size distribution were calculated from the size analyses given in appendix 1. Plots of the log of the size vs. the cumulative percentage yielded nearly straight lines over most of the probability range. This indicated that the size could be adequately represented as a log-normal distribution.

$$f(\log L) = \frac{1}{\sqrt{2\pi}\,\log \sigma'} \exp \frac{-\log^2(L/\bar{L}')}{2\,\log^2 \sigma'} \tag{4.2}$$

$$\bar{L}' = L_{0.05} \tag{4.3}$$

$$\sigma' = L_{.841}/L_{0.5} \tag{4.4}$$

For the log-normal distribution, the population-weighted mean size was calculated by (32)

$$\bar{L} = L_{0.50} \exp\,(\tfrac{1}{2} \log^2\sigma') \tag{4.5}$$

The measure of size distribution was the coefficient of variation which was a measure of the dispersity and was calculated by

$$\text{c.v.} = [\exp(\log^2\sigma')-1]^{\frac{1}{2}} \tag{4.6}$$

The models for size and size distribution have been presented in Tables 4.14 to 4.16. For the central composite design, no effects were deemed important for the size distribution. Observation under the microscope indicated that a large amount of agglomeration had occurred. The image analysis technique could not distinguish between individual particles within the agglomerate and therefore measured the agglomerated particle as a single entity. The implication was that the measured particle sizes were much larger than the true particle size. Time was not a significant variable for determining the particle size as would be expected from crystal growth or agglomeration theory. Instead, the agglomeration was most likely due to the washing and drying of the filtercake before the sample was mounted on a slide. The samples of some of the runs were mounted directly upon the slides from the solution. The particles observed under the microscope for these cases were of a uniform size and below 1 micrometer in diameter. When these samples were washed and dried as before, the agglomeration occurred. The unwashed particles were too small to be analyzed by the image analysis technique. the effect of sulphate and peroxide levels upon the size and size distribution was more of an effect upon the caking properties than the true particle size. The results of the particle size analysis indicated that a different method should be employed for measuring sizes and distributions, i.e. light scattering or electron photomicrographic techniques.

FILTRATION RATES

One processing variable that can be expected to be of importance in yellow cake processing is the slurry filtration rate. In this investigation with the exception of two runs, filtration rates were rapid, i.e. no more than two or three minutes. Consequently no significant measurements could be made. This is indicative of a strong crystalline structure in the filter cake such that no filter pore or interstructual blocking took place. Such conditions can be

Table 4.14

Plausible Models for the Mean Particle Size
For Experimental Plan I

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	95	β_0	11.100	778.288	25.943
1/2	80,90	β_0	11.090±1.769	673.077	23.210
		β_4	2.094±2.011		
3/1	all	β_0	11.100	778.288	25.943

Q-test Results

Model A	Model B	Q	F
1/1	1/2	4.53	4.18

R-test Results

Case/Model	R	F
1/2	3.64	5.79

Table 4.15

Plausible Models for Mean Particle Size
for Experimental Plan II

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	10.177± .752	284.319	15.796
		β_4	3.266± .987		
		β_{24}	- 2.203± .987		
3/1	all	β_0	10.177±1.999	363.861	19.150
		β_4*	5.316±3.748		

R-test Results

Case/Model	R	F
1/1	2.58	5.87
3/1	3.17	5.86

Table 4.16

Plausible Models for the Size Distribution for Experimental Plan II

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	.487± .083	.629	.033
		β_4	- .102± .095		
3/1	90	β_0	.427± .071	.408	.019
		β_4*	- .140± .116		
		β_{12}*	.186± .142		
		β_{35}	.204± .122		
3/2	95	β_0	.487	.791	.040

Q-test Results

Model A	Model B	Q	F
3/2	3/1	6.72	3.20

R-test Results

Case/Model	R	F
1/1	6.72	5.85
3/1	4.92	5.90

considered of great advantage in any filtration process. However in the case of run number 10 and 19 filtration rates were approximately 40 minutes. Both of these runs were characterized by high sulphate concentrations and particle sizes and size distributions were examined. The size distributions for runs 10 and 19 were significantly different than for all the other runs. Also while the size distribution was characterized by large agglomerates, the individual particle sizes were very small and that under these conditions very fine crystals were formed which would be capable of hindering filtration. A further study should be taken to determine whether high sulphate concentrations could result in poor filtration rates especially in the absence of insufficient peroxide to precipitate all the uranium present.

5. CONCLUSIONS AND RECOMMENDATIONS

The results of this investigation can be summarized as follows:

1) The preparation of high quality yellow cake from uranyl sulphate solutions can be readily carried out using hydrogen peroxide. Precipitation rates were rapid, yields were high and the resultant crystal slurry exhibited good handling characteristics confirming reports published in the literature (3,21).

2) In the presence of the stoichiometric ratio or greater of hydrogen peroxide to uranium the quantity of uranium precipitated and the filter cake yield can be adequately represented by a simple linear model involving the initial uranium concentration. This would permit simple control of the process by the uranium mill operator to obtain a product meeting refiners' standards with respect to uranium and sulphate.

3) The two major processing variables that will effect yield and product quality are the peroxide to uranium ratio and the sulphate level. Thus insufficient peroxide and high sulphate levels will result in lower product quality.

Poor slurry handling characteristics as evidenced by excessive filtration times could also be encountered. The effect of the variables at these levels made it impossible to use linear modelling techniques over the entire operational range.

4) Linear modelling could not be used to represent the barrens data. However for this method of preparing yellow cake it would be expected that barrens concentrations less than 0.005 g/l could be readily obtained.

5) The precipitation pH although not highly significant in the linear modelling had the following effects. Thus when pH was increased:

   i) the filtercake yield increased

   ii) the barrens concentration was lowered

   iii) the uranium content of the cake was lower

   iv) the conversion increased

   v) the sulphate content of cake decreased.

6) Time proved to be an insignificant variable at the sulphate levels studied with respect to the yield. However, a minimum precipitation time may be needed to reach a required barrens concentration.

7) The results obtained with the outlying points showed that to take into account the effects of operating away from optimum precipitation conditions non linear modelling techniques would have to be used.

8) Any study of the actual kinetics of the uranium-hydrogen peroxide reaction would have to be carried out at high sulphate levels so that the appropriate kinetic equation could be developed.

Recommendations for future work are as follows:

1) A detailed study of the actual precipitation mechanism and the inhibiting effect of sulphate so that a kinetic equation can be developed for predicting yields and barrens concentrations. It would be also useful to have a

knowledge of the effect of precipitation temperature on conversions and crystal growth. It is also recommended to avoid parameter interaction that the runs be carried out in a continuous precipitator so that better control of the pH can be achieved.

2) A study should be made of the ammonium diuranate precipitation reaction using linear modelling techniques employed in this study. Initial runs should be carried out over a relatively small range of variables to avoid problems encountered in this study. Such a study could prove useful in identifying feasible operating models for this system. Again it is recommended a continuous precipitator be used.

6. REFERENCES

1. Ritcey, G.M., Ashbrook, A.W., "Solvent Extraction, Principles and Application to Process Metallurgy, Part 2", pp. 452-522, Elsevier Scientific Publishing Co., Amsterdam, (1979).
2. Boydell, D.W., "Production of Yellowcake and Uranium Fluorides", Proc. of an Advisory Group Meeting, Paris, 5-8 June 1979, p. 29, IAEA, Vienna (1980).
3. Litz, J.E., Coleman, R.B., ibid, Page 101.
4. Alfredson, P.G., ibid, Page 149.
5. Ritcey, G.M., Ashbrook, A.W., "Solvent Extraction, Principles and Application to Process Metallurgy, Part 2", Page 427, Elsevier Scientific Publishing Co., Amsterdam, (1979).
6. ibid, p. 486 (1979).
7. op.cit., p. 454 (1979).
8. Boydell, D.W., "Production of Yellowcake and Uranium Fluorides", p. 40 (1980).
9. ibid, p. 46 (1980).

10. Ritcey, G.M., Ashbrook, A.W., "Solvent Extraction, Principles and Application to Process Metallurgy, Part 2", pp. 457 (1979).

11. ibid, p. 464 (1979).

12. Brown, R.A., "The Precipitation of Uranium with Hydrogen Peroxide", FMC Corp., Chemical Research and Development Centre, Princeton, N.J. (1980).

13. Tomazic, B., Samarzija, M. and Branica, M., J. Inorg. Nucl. Chem., 31, 1771 (1969).

14. Stuart, W.L. and Whateley, T.L., J. Inorg, Nucl. Chem., 31, 1639 (1969).

15. Merino, J.L., "Production of Yellowcake and Uranium Fluorides", Proc. of an Advisory Group Meeting, Paris, 5-8 June 1979, p. 63, IAEA, Vienna, (1980).

16. Rodriguez, B., ibid, p. 83.

17. Bryson, A.W., J. S. Afr. Inst. Min. and Met., Sept. 1975, p. 13.

18. Shabbir, M. and Tame, J.E., U.S. Bureau of Mines Report of Investigation 1974, R1-7931.

19. Bhattacharyya, P.K., Saini, R.D., Ruikar, P.B., Intl. J. Chem. Kin., 14, 1219 (1982).

20. Bhattacharyya, P.K., Saini, R.D., Ruikar, P.B., Intl. J. Chem. Kin., 13, 385 (1981).

21. Caropreso, F.E. and Badger, W.P., Trans. Soc. Min. Eng., AIME, Dec. 1973, p. 281 (1973).

22. Kresin, P., "Hydrogen Peroxide Precipitation of Uranium, A Laboratory Study", Madawaska Mines (1981).

23. Randolph, A.D. and Larson, M.A., "Theory of Particulate Processes, Analysis and Techniques of Continuous Crystallization", Academic Press (1971).

24. Bacon, D.W., "Collection and Interpretation of Industrial Data"

NOMENCLATURE

A	Surface Area of a Crystal, cm^2
C	Concentration of the crystallizing species in the bulk solution, moles/l
C_i	Concentration of the crystallizing species at the liquid-solid interface, moles/l
C^*	Solubility of the crystallizing species, moles/l
$\underline{C}$	Variance-Covariance matrix of the parameter estimates
c.v.	Coefficient of Variation
D_p	Particle Diameter, μm
e_u	Residual value for run u
F_{ν^1,ν^2}	Value of F-distribution for ν^1 and ν^2 degrees of freedom
k_d	Diffusion mass transfer coefficient, Eq. 1.2.1 (g.1)/(sec)(cm^2)(mol)
k_{obs}	Observed reaction rate constant Eq. 1.1.6 $(mole)^{-1}$ $(time)^{-1}$
k_r	Surface reaction mass transfer coefficient, Eq. 1.2.2 (g.1)/(sec)(cm^2)(mol)
K_{dec}	Decomposition rate of H_2O_2, (moles) $(time)^{-33}$, Eq. 1.1.4
K_G	Overall mass transfer coefficient, Eq. 1.2.3 (g.1)/(sec)(cm^2)(mol)
$K_{H_2O_2}$	Equilibrium constant Eq. 1.1.2
K_0	Initial value of $K_{H_2O_2}$, Eq. 1.1.3
$\bar{L}$	Mean particle size, μm
$\bar{L}'$	Adjustable mean length parameter in a log-normal distribution, μm
$L_{.50}$	Median particle size, μm
m	Mass of a crystal Equations 1.2.1 - 1.2.3, g
m	Number of centrepoint runs for the factorial design
n	Number of experimental runs

p	Number of parameters in the linear equation
Q	Ratio of extra sum of squares to the estimated variance
r	Radius of a crystal, cm, Eq. 1.2.5
R	Ratio of error due to lack of fit to the pure error variance
SSR	Sum of squares of the residuals
t	Time, sec
t_ν	Value of t-distribution for ν degrees of freedom
U_0	Initial uranium concentration, g/l
x_i	Coded value of independent variable i in the linear equations
x_{iu}	Coded value of independent variable i for run u
X_i	Actual value of the independent variable i
$\underline{X}$	Matrix of the independent variables
Y_u	Measured response for experimental run u
Y	Dependent variable in the linear equation
$\underline{Y}$	Vector of measured responses

GREEK SYMBOLS

β_i	Parameter associated with main effect i in the linear equation i = 0,1,2,...,5
β_{ii}	Parameter associated with a quadratic effect i i = 1,2,...,5
β_{ij}	Parameter associated with an interaction effect between variables i and j i,j = 1,2,...,5, i≠j
$\hat{\beta}$	Parameter value estimated from linear least squares
$\underline{\hat{\beta}}$	Vector of estimated parameter values
ϵ	Random error associated with a measured response
ν	Degrees of freedom for a t-distribution

ν_1	Degrees of freedom in the numerator of an F-distribution
ν_2	Degrees of freedom in the denominator of an f-distribution
ρ	Density of a crystal, g/cm^3 Eq. 1.2.5
σ^1	Adjustable dispersion parameter in a log-normal distribution
σ^2	Estimated variance

SUPERSCRIPTS

T	Transpose of a matrix
*	Solubility value, Equations 1.2.2 - 1.2.5
*	Alternative set of independent variables in the linear equations, Cases 2 and 4

SUBSCRIPTS

0	Initial value
0	Value of y-intercept in the linear equations
1	Initial Uranium Content
2	Amount of H_2O_2
3	pH
4	Sulphate Level
5	Time
c.p.	Centrepoint

APPENDIX A

TABLE A-1

EXPERIMENTAL RESULTS

Run Number	Filtercake Yield (g)	Uranium Precipated (g)	Barrens Concentration (g U/1)	Conversion (%)
1	18.86	11.799	.061	96.952
2	26.81	16.445	.160	96.526
3	19.71	12.039	.045	97.976
4	27.67	16.879	.0022	98.217
5	19.93	11.787	.0001	97.144
6	28.57	16.931	.0002	98.371
7	20.17	11.697	.0002	96.784
8	28.25	16.636	.0001	97.531
9	19.87	11.688	.0065	96.728
10	25.08	15.121	1.57	88.714
11	19.44	11.831	.029	97.208
12	27.11	16.689	.010	97.651
13	19.81	11.605	.0003	96.416
14	28.11	16.031	.0005	95.800
15	19.81	11.951	.0074	97.776
16	28.45	16.882	.0005	98.234
17	16.06	8.899	.026	94.360
18	31.83	19.178	.023	97.885
19	12.62	7.352	6.24	53.710
20	24.63	14.576	.060	98.387

TABLE A-1(Cont'd)

Run Number	Filtercake Yield (g)	Uranium Precipated (g)	Barrens Concentration (g U/1)	Conversion (%)
21	20.70	13.546	.640	93.020
22	24.63	14.603	.0032	98.667
23	24.06	14.501	.0049	98.320
24	24.43	14.331	.0004	97.767
25	24.78	14.231	.0033	97.427
26	21.98	13.597	.0008	98.653
27	22.88	14.035	.013	96.727
28	24.41	14.348	.0004	97.827
29	23.87	14.42	.002	98.060
30	23.42	13.895	.0019	99.647
31	24.19	14.490	.0001	98.300
32	23.00	14.433	.0001	98.107
33	24.19	14.485	.0023	98.273
34	24.81	15.362	.0006	101.207
35	23.74	14.348	.0015	97.820
36	24.42	14.53	.0008	98.433

TABLE A-2

EXPERIMENTAL RESULTS

Run Number	Uranium Content of Cake (%)	Sulphur Content of Cake (%)	Mean Particle Size (μ)	Particle Size Distribution Coefficient of Variation
1	62.56	.25	5.59	.43
2	61.34	.14	7.03	.74
3	61.08	.13	8.82	.58
4	61.00	.29	5.88	.91
5	59.14	.10	4.86	.52
6	59.26	.10	7.36	.33
7	58.00	.35	6.90	.80
8	58.89	.20	12.05	.65
9	58.82	.63	14.29	.45
10	60.29	.53	28.59	.02
11	60.86	.15	8.22	.35
12	61.56	.18	8.70	.51
13	58.58	.26	14.31	.62
14	57.03	.37	11.42	.66
15	60.33	.15	13.63	.35
16	59.34	.14	11.61	.37
17	55.41	.07	18.37	.35
18	60.25	.29	9.07	.42
19	58.26	.44	20.46	.23

TABLE A-2

EXPERIMENTAL RESULTS

Run Number	Uranium Content of Cake (%)	Sulphur Content of Cake (%)	Mean Particle Size (μ)	Particle Size Distribution Coefficient of Variation
20	59.18	.22	10.82	.34
21	65.44	.10	8.36	.42
22	59.29	.18	19.23	.28
23	60.27	.17	11.21	.39
24	58.66	.12	10.21	.47
25	57.43	.72	9.11	.45
26	61.86	.21	13.24	.29
27	61.34	.16	10.85	.43
28	58.78	.22	-	-
29	60.41	.40	12.61	.27
30	59.33	.22	-	-
31	59.90	.08	6.09	.45
32	62.59	.20	-	-
33	59.88	.24	6.27	.36
34	61.92	.26	-	-
35	60.44	.15	9.20	.43
36	59.50	.23	-	-

TABLE A-3

PARTICLE SIZE DISTRIBUTIONS

Run Number	$D_{p_{\mu m}}$	Cumulative %	Difference %
1	1.67	9.02	9.02
	2.35	18.70	9.68
	3.30	40.22	21.52
	4.70	56.56	16.34
	6.60	75.36	18.80
	9.40	87.73	12.37
	13.20	96.29	8.56
	18.60	97.90	1.61
	26.30	100.00	2.10
2	1.67	3.65	3.65
	2.35	21.65	18.00
	3.30	39.18	17.53
	4.70	56.02	16.84
	6.60	65.07	9.05
	9.40	72.50	7.43
	13.20	79.76	7.26
	18.60	85.09	5.33
	26.30	91.94	6.85
	37.10	100.00	8.06
3	1.67	6.78	6.78
	2.35	17.20	10.41
	3.30	26.67	9.47
	4.70	44.59	17.92
	6.60	59.60	15.01
	9.40	72.10	12.50
	13.20	79.18	7.07
	18.60	84.46	5.28
	26.30	86.47	2.01
	37.10	100.00	13.53
4	1.67	1.25	1.25
	2.35	22.91	21.66
	3.30	48.31	25.40
	4.70	67.02	18.71
	6.60	76.68	9.66
	9.40	81.14	4.46
	13.20	82.69	1.55
	18.60	89.22	6.62
	26.30	91.93	2.71
	37.10	100.00	8.07

TABLE A-3(Cont'd)

Run Number	$D_{p_{\mu m}}$	Cumulative %	Difference %
5	1.67	5.86	5.86
	2.35	26.13	20.27
	3.30	51.72	25.59
	4.70	69.73	18.01
	6.60	81.24	11.51
	9.40	87.21	5.97
	13.20	91.12	3.91
	18.60	96.39	5.27
	26.30	100.00	3.61
6	1.67	2.51	2.51
	2.35	9.99	7.48
	3.30	22.00	12.01
	4.70	38.66	16.66
	6.60	61.35	22.69
	9.40	78.26	16.91
	13.20	89.24	10.98
	18.60	94.67	5.43
	26.30	96.44	1.77
	37.10	100.00	3.56
7	1.67	4.61	4.61
	2.35	17.94	13.33
	3.30	42.54	24.60
	4.70	56.27	13.73
	6.60	71.75	15.48
	9.40	74.81	3.05
	13.20	83.05	8.25
	18.60	86.86	3.81
	26.30	92.31	5.45
	37.10	100.00	7.69
8	1.67	-4.34	-4.34
	2.35	6.61	10.94
	3.30	26.95	20.34
	4.70	31.20	4.26
	6.60	51.81	20.61
	9.40	58.44	6.63
	13.20	64.88	6.44
	18.60	68.93	4.05
	26.30	68.99	0.06
	37.10	100.00	31.01

TABLE A-3(Cont'd)

Run Number	$D_{p_{\mu m}}$	Cumulative %	Difference %
9	1.67	-6.64	- 6.64
	2.35	-1.34	5.30
	3.30	11.94	13.29
	4.70	27.27	15.33
	6.60	39.39	12.13
	9.40	53.09	13.70
	13.20	63.97	10.88
	18.60	67.37	3.40
	26.30	77.27	9.90
	37.10	100.00	22.73
10	1.67	5.65	5.65
	2.35	5.70	0.05
	3.30	7.70	2.00
	4.70	6.90	-0.80
	6.60	5.00	-1.90
	9.40	8.39	3.39
	13.20	10.90	2.51
	18.60	11.20	0.30
	26.30	29.35	18.15
	37.10	100.00	70.65
11	1.18	1.21	1.21
	1.67	2.52	1.30
	2.35	4.58	2.06
	3.30	14.07	9.48
	4.70	35.10	21.04
	6.60	57.81	22.71
	9.40	76.23	18.42
	13.20	86.07	9.83
	18.60	91.84	5.77
	26.30	95.70	3.87
	37.10	98.10	2.40
	52.40	98.62	.52
	74.00	100.00	1.38
12	1.67	9.13	9.13
	2.35	17.64	8.51
	3.30	30.47	12.83
	4.70	45.03	14.56
	6.60	56.74	11.71
	9.40	69.07	12.33
	13.20	79.00	9.93
	18.60	86.49	7.49
	26.30	100.00	13.51

TABLE A-3(Cont'd)

Run Number	$D_{p_{\mu m}}$	Cumulative %	Difference %
13	1.18	3.83	3.83
	1.67	5.33	1.50
	2.35	6.51	1.18
	3.30	11.06	4.55
	4.70	26.55	15.49
	6.60	46.46	19.92
	9.40	61.32	14.85
	13.20	69.64	8.32
	18.60	75.06	5.42
	26.30	80.51	5.45
	37.10	84.47	3.96
	52.40	88.13	3.66
	74.00	90.31	2.18
	104.00	96.60	6.28
	147.00	100.00	3.40
14	1.18	2.80	2.80
	1.67	4.47	1.67
	2.35	7.53	3.06
	3.30	19.64	12.11
	4.70	36.98	17.34
	6.60	53.84	16.85
	9.40	65.84	12.00
	13.20	69.79	3.95
	18.60	75.38	5.58
	26.30	83.09	7.71
	37.10	89.06	5.97
	52.40	93.14	4.08
	74.00	96.13	2.99
	104.00	100.00	3.87
15	1.18	2.91	2.91
	1.67	6.25	3.33
	2.35	4.23	-2.02
	3.30	6.17	1.94
	4.70	15.14	8.97
	6.60	32.06	16.92
	9.40	51.59	19.53
	13.20	67.67	16.08
	18.60	80.01	12.35
	26.30	87.65	7.63
	37.10	92.97	5.33
	52.40	95.03	2.06
	74.00	98.04	3.01
	104.00	100.00	1.96

TABLE A-3(Cont'd)

Run Number	$D_{p_{\mu m}}$	Cumulative %	Difference %
16	1.18	2.58	2.58
	1.67	3.75	1.16
	2.35	3.36	-0.39
	3.30	8.88	5.52
	4.70	19.76	10.88
	6.60	40.69	20.93
	9.40	59.99	19.30
	13.20	75.14	15.15
	18.60	84.52	9.37
	26.30	90.26	5.74
	37.10	94.16	3.90
	52.40	97.81	3.66
	74.00	100.00	2.19
17	1.18	3.81	3.81
	1.67	1.67	-2.14
	2.35	3.93	2.26
	3.30	10.78	6.85
	4.70	20.16	9.38
	6.60	33.75	13.59
	9.40	43.12	9.37
	13.20	52.43	9.31
	18.60	61.96	9.53
	26.30	74.90	12.94
	37.10	91.00	16.10
	52.40	97.35	6.35
	74.00	100.00	2.65
18	1.18	7.91	7.91
	1.67	11.72	3.81
	2.35	14.81	3.08
	3.30	19.37	4.56
	4.70	35.76	16.40
	6.60	55.93	20.16
	9.40	72.62	16.69
	13.20	81.80	9.18
	18.60	86.43	4.63
	26.30	92.00	5.58
	37.10	95.51	3.50
	52.40	98.89	3.39
	74.00	100.00	1.11

TABLE A-3(Cont'd)

Run Number	$D_{p_{\mu m}}$	Cumulative %	Difference %
19	1.18	1.43	1.43
	1.67	3.04	1.61
	2.35	3.70	0.65
	3.30	6.67	2.97
	4.70	12.27	5.60
	6.60	21.42	9.15
	9.40	32.64	11.22
	13.20	45.05	12.42
	18.60	61.68	16.62
	26.30	77.67	16.00
	37.10	90.48	12.81
	52.40	97.15	6.67
	74.00	100.00	2.85
20	1.18	3.44	3.44
	1.67	4.49	1.05
	2.35	6.54	2.05
	3.30	11.32	4.78
	4.70	24.85	13.53
	6.60	43.88	19.03
	9.40	61.56	17.68
	13.20	78.04	16.78
	18.60	89.00	10.96
	26.30	92.23	3.23
	37.10	95.29	3.06
	52.40	97.40	2.11
	74.00	98.74	1.34
	104.00	100.00	1.26
21	1.18	9.91	9.91
	1.67	13.46	3.55
	2.35	18.62	5.16
	3.30	26.65	8.03
	4.70	39.43	12.78
	6.60	58.20	18.77
	9.40	71.83	13.63
	13.20	83.43	11.61
	18.60	90.88	7.45
	26.30	95.29	4.41
	37.10	99.36	4.07
	52.00	100.00	0.64

TABLE A-3(Cont'd)

Run Number	$D_{p_{\mu m}}$	Cumulative %	Difference %
22	1.18	2.70	2.70
	1.67	5.00	2.30
	2.35	7.87	2.87
	3.30	12.51	4.64
	4.70	24.97	12.46
	6.60	39.41	14.44
	9.40	59.62	20.21
	13.20	78.22	18.60
	18.60	90.02	11.80
	26.30	97.21	7.18
	37.10	99.58	2.38
	52.40	100.00	0.42
23	1.18	5.84	5.84
	1.67	6.08	0.23
	2.35	8.66	2.59
	3.30	12.66	4.00
	4.70	26.99	14.33
	6.60	44.63	17.64
	9.40	63.19	18.56
	13.20	78.43	15.23
	18.60	87.64	9.22
	26.30	94.02	6.37
	37.10	97.55	3.53
	74.00	100.00	2.45
24	1.18	2.91	2.91
	1.67	4.19	1.29
	2.35	5.81	1.62
	3.30	14.50	8.69
	4.70	31.29	16.79
	6.60	51.21	19.91
	9.40	67.81	16.60
	13.20	77.96	10.15
	18.60	84.84	6.88
	26.30	90.04	5.20
	37.10	97.71	7.67
	52.40	100.00	2.29

TABLE A-3(Cont'd)

Run Number	$D_{p_{\mu m}}$	Cumulative %	Difference %
25	1.18	3.55	3.55
	1.67	5.83	2.27
	2.35	8.39	2.57
	3.30	16.05	7.65
	4.70	34.81	18.76
	6.60	56.89	22.08
	9.40	72.24	15.35
	13.20	80.94	8.70
	18.60	85.22	4.29
	26.30	89.70	4.48
	37.10	92.54	2.84
	52.40	97.79	5.25
	74.00	98.59	0.80
	104.00	100.00	1.41
26	1.18	2.64	2.64
	1.67	4.97	2.34
	2.35	4.99	0.02
	3.30	9.72	4.73
	4.70	20.76	11.04
	6.60	34.87	14.11
	9.40	50.29	15.42
	13.20	69.41	19.12
	18.60	83.08	13.67
	26.30	89.23	6.15
	37.10	95.94	6.71
	52.40	98.94	3.01
	74.00	100.00	1.06
27	1.18	2.64	2.64
	1.67	5.58	2.95
	2.35	8.30	2.72
	3.30	13.64	5.34
	4.70	28.22	14.57
	6.60	47.52	19.31
	9.40	64.58	17.06
	13.20	77.51	12.93
	18.60	83.70	6.19
	26.30	87.25	3.55
	37.10	91.55	4.30
	52.40	94.57	3.02
	74.00	97.34	2.77
	104.00	100.00	2.66

TABLE A-3(Cont'd)

Run Number	$D_{p_{\mu m}}$	Cumulative %	Difference %
29	1.18	-0.15	-0.15
	1.67	1.67	1.82
	2.35	0.90	-0.77
	3.30	5.22	4.33
	4.70	17.67	12.44
	6.60	33.58	15.92
	9.40	54.52	20.93
	13.20	74.30	19.79
	18.60	87.00	12.70
	26.30	93.45	6.45
	37.10	97.18	3.73
	52.40	99.30	2.12
	74.00	100.00	0.70
31	1.18	6.13	6.13
	1.67	12.34	6.21
	2.35	14.77	2.43
	3.30	31.65	16.88
	4.70	56.07	24.42
	6.60	74.07	18.01
	9.40	84.04	9.97
	13.20	88.61	4.57
	18.60	91.40	2.79
	26.30	94.08	2.67
	37.10	96.21	2.13
	52.40	96.16	-0.05
	74.00	100.00	3.84
33	1.18	4.97	4.97
	1.67	10.38	5.40
	2.35	14.50	4.12
	3.30	26.07	11.57
	4.70	51.33	25.26
	6.60	73.43	22.10
	9.40	87.53	14.10
	13.20	93.22	5.69
	18.60	95.96	2.75
	26.30	98.43	2.46
	37.10	99.45	1.02
	52.40	100.00	0.55

TABLE A-3(Cont'd)

Run Number	$D_{p_{\mu m}}$	Cumulative %	Difference %
35	1.18	8.33	8.33
	1.67	6.75	-1.58
	2.35	11.70	4.94
	3.30	20.44	8.74
	4.70	36.02	15.58
	6.60	55.02	19.27
	9.40	69.23	13.94
	13.20	80.31	11.08
	18.60	87.87	7.56
	26.30	94.74	6.86
	37.10	99.15	4.42
	52.40	100.00	0.85